

EXHIBIT 4

ENVIRONMENTAL ORGANIC CHEMISTRY

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CHAPTER 11

SORPTION: SOLID-AQUEOUS SOLUTION EXCHANGE

11.1 INTRODUCTION

The process in which chemicals become associated with solid phases is generally referred to as *sorption* (either *adsorption* onto a two-dimensional surface, or *absorption* into a three-dimensional matrix). This phase transfer process may involve interacting either vapor molecules or dissolved molecules with adjacent solid phases.

Sorption is extremely important because it may dramatically affect the fate and impact of chemicals in the environment. Such importance is readily understood if we recognize that structurally identical molecules behave very differently if they are surrounded by water molecules and ions as opposed to clinging onto the exterior of solids or being buried within a solid matrix (Fig. 11.1). Clearly, the environmental movements of water-borne molecules must differ from that fraction of the same kind of molecules carried by particles that settle. Additionally, only the dissolved molecules are available to collide with the interfaces leading to other environmental compartments such as air; and thus these phase transfers, for practical purposes, are limited to the dissolved species of a chemical. Finally, the chemical milieu of the solution and solid worlds differ greatly. For example, the thin layer of water surrounding silicate surfaces is typically "more acidic" than bulk water, and thus reactions involving protons or hydroxide ions proceed at different rates for sorbed molecules which are otherwise structurally identical to dissolved molecules. It is possible that molecules located within particles are substantially shaded from incident light; therefore, these molecules may not get involved with direct photochemical processes or short-lived reactive species such as $\cdot\text{OH}$ (see Chapter 13). Finally insofar as molecular transfer into microorganisms is frequently a prerequisite to a substance's biodegradation, it

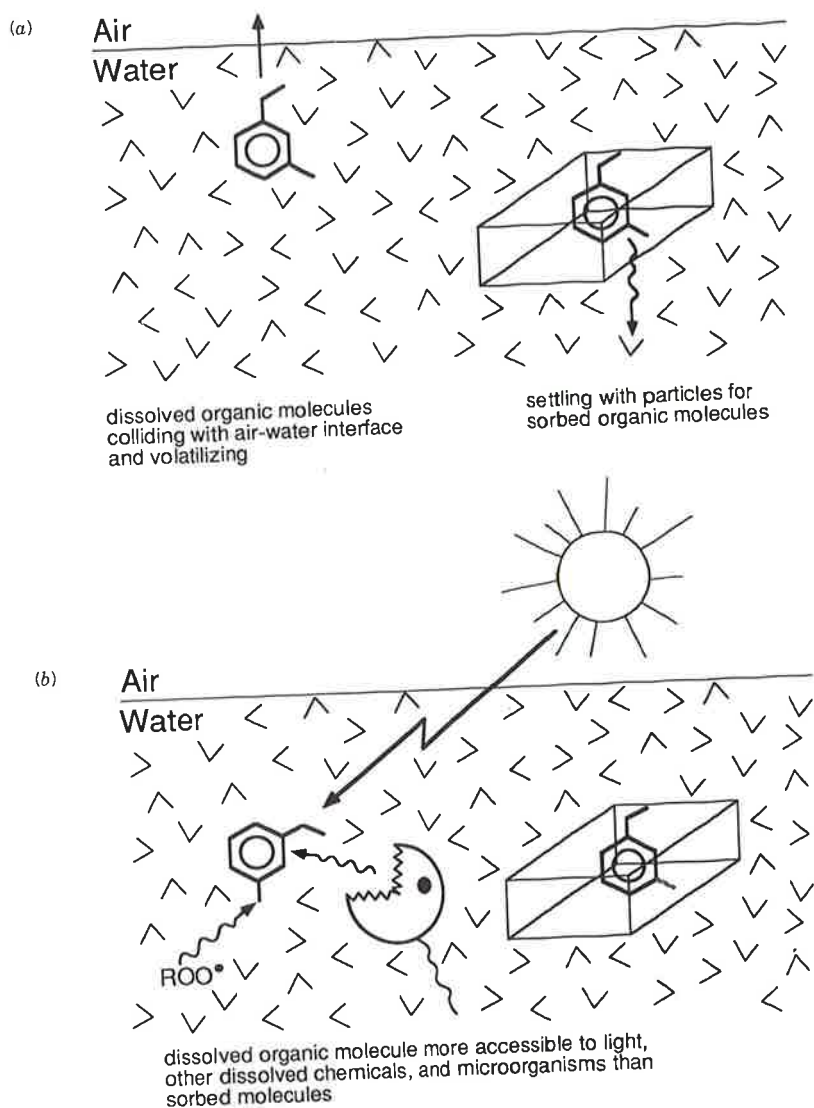


Figure 11.1 Some processes in which sorbed species behave differently than dissolved molecules of the same substance. (a) For example, dissolved species may undergo air-water exchange while sorbed species may sediment. (b) Also, dissolved species may react at different rates as compared to their sorbed counterparts.

should be recognized that the greater ease of chemical movement from solution versus from within solids to bacteria generally causes the biological decomposition of the sorbed form of the chemical to be slower than its dissolved counterpart. Hence, we must understand solid-solution exchange phenomena before we can quantify virtually any other process affecting the fate of chemicals in the environment.

Unfortunately, sorption is not always a single simple process (Westfall, 1987). Rather, some combination of interactions may be responsible for governing the association of any particular chemical (called a *sorbate*) with any particular solid (called a *sorbent*). Figure 11.2 illustrates this point for 4-chloroaniline (4-chloroaminobenzene). First, chiefly because of unfavorable free-energy costs of remaining in aqueous solution, such an organic substance may escape the water by penetrating

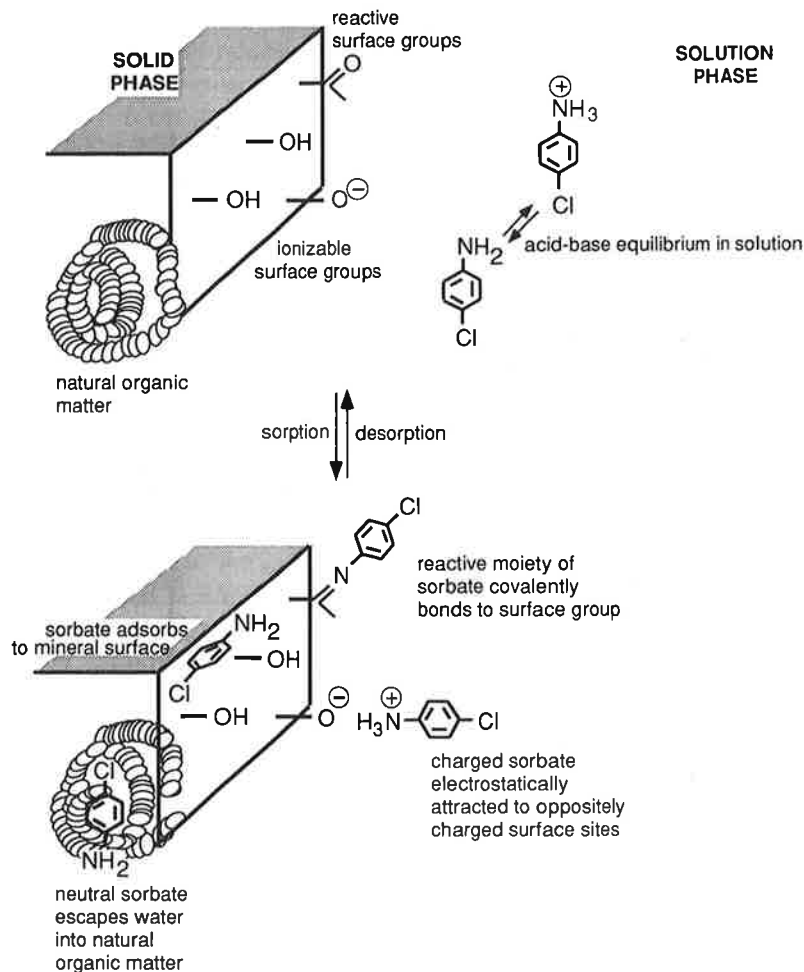


Figure 11.2 Some sorbent-sorbate interactions possibly controlling the association of a chemical with particles.

natural organic matter in the particulate phase. Additionally, such a molecule may displace water molecules from the region near the mineral surface to some extent and thereby be associated with the surface via van der Waals, dipole-dipole, and other weak intermolecular forces. These two mechanisms of sorption are general and will operate for any organic chemical and any natural solid. Additionally, if the sorbate is ionizable in the aqueous solution, then attraction to specific surface sites exhibiting the opposite charge will promote sorption of the ionic species. Finally, should the sorbate and sorbent exhibit mutually reactive moieties (e.g., in Fig. 11-2 a carbonyl group on the sorbent and an amino group on the sorbate), some portion of the chemical may actually become bonded to the solid. All of these interaction mechanisms will operate simultaneously, and the combination that dominates the overall solution-solid distribution will depend on the structural properties of the organic chemical and solid medium of interest.

In this chapter we try to visualize the sets of molecular interactions involved in each of the sorption processes. This means that we have to consider van der Waals and dipole-dipole interactions, H-bonding, ionic interactions between charged species, and specific bonding of reactive moieties and solid surface atoms or groups. With such pictures in our minds, we will seek to understand what makes various sorption mechanisms important under various circumstances. Establishing the critical molecular properties and solid characteristics will enable us to understand why certain predictive approaches may be applied. Ultimately, we should gain some feeling for what structural features of a chemical and what characteristics of solids (and solutions) are important to sorption interactions. Finally, we conclude by examining the factors limiting the rate of approach to sorption equilibrium.

11.2 QUANTIFYING THE RELATIVE ABUNDANCES OF DISSOLVED AND SORBED SPECIES: THE SOLID-WATER DISTRIBUTION RATIO K_d

When we are interested in assessing the *equilibrium* proportion of a particular chemical's presence in association with solids for any particular volume of an aquatic environment, we begin by considering how the total sorbate concentration associated with the sorbent, C_s ($\text{mol} \cdot \text{kg}^{-1}$), depends on the total chemical concentration in the solution, C_w ($\text{mol} \cdot \text{L}^{-1}$). Such a relationship is commonly referred to as a *sorption isotherm*. The term isotherm is used to indicate that one is considering sorption at a constant temperature. Depending on the dominating mechanism(s), sorption isotherms may exhibit different shapes (Fig. 11.3). Experimentally determined isotherms can commonly be fit with a relationship of the form

$$C_s = K \cdot C_w^n \quad (11-1)$$

This equation is known as the Freundlich isotherm; K is referred to as the Freundlich constant; and n is a measure of the nonlinearity involved. Case I in Figure 11.3 ($n < 1$) reflects the situation in which at higher and higher sorbate concentrations, it becomes more and more difficult to sorb additional molecules. This may occur in cases where

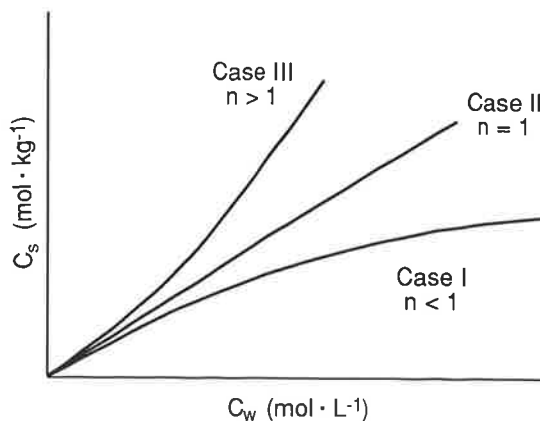


Figure 11.3 Three types of observed relationships between concentrations of a chemical in the sorbed state, C_s , and the dissolved state, C_w . All can be fit with a relationship of the form $C_s = K \cdot C_w^n$ where K and n are constants.

specific binding sites become filled or remaining sites are less attractive to the sorbate molecules. Case III ($n > 1$) describes a contrasting situation in which previously sorbed molecules lead to a modification of the surface which favors further sorption. Such effects have been seen for surface active compounds like alkyl benzene sulfonates (see Table 2.6), where the sorbent becomes coated and increasingly exhibits a nonpolar nature. Finally, Case II ($n = 1$) reflects those situations in which the attractiveness of the solid for the sorbates remains the same for all levels of C_s . This is the so-called *linear isotherm* case; one should also realize that over narrow ranges in C_w , particularly at low concentrations, both Cases I and III appear to be linear.

Let us now consider a case in which we know the *ratio* of a substance's total equilibrium concentrations in the sorbed phase and in the solution. We denote this distribution ratio with K_d :

$$K_d = \frac{C_s}{C_w} \quad \frac{(\text{mol} \cdot \text{kg}^{-1})}{(\text{mol} \cdot \text{L}^{-1})} \quad (11-2)$$

The value of this ratio may only apply at the given solute concentration (i.e., n in Eq. 11-1 may not equal 1). In fact, inserting Eq. 11-1 into Eq. 11-2 yields

$$K_d = K \cdot C_w^{n-1} \quad (11-2a)$$

Often, one assumes that K_d is constant over some concentration range. From Eq. 11-2a we can differentiate K_d with respect to C_w , rearrange the result, and find

$$\frac{dK_d}{K_d} = (n - 1) \frac{dC_w}{C_w} \quad (11-2b)$$

so this assumption about the constancy of K_d is equivalent to presuming: (a) the overall sorption process is either described by a linear isotherm ($n = 1$ in Eq. 11-1), or (b) the relative concentration variation, dC_w/C_w , is sufficiently small to guarantee that the relative K_d variation, dK_d/K_d , is also small.

Armed with such a K_d parameter for a case of interest, we may evaluate what fraction of a compound is in the water solution, f_w , in a volume containing both solids and water (but only these phases):

$$f_w = \frac{C_w \cdot V_w}{C_w V_w + C_s M_s} \quad (11-3)$$

where V_w is the volume of water (L) in total volume V_{tot} , and M_s is the mass of solids (kg) present in that same total volume. Now if we substitute the product $K_d \cdot C_w$ from Eq. 11-2 for C_s in Eq. 11-3, we have

$$\begin{aligned} f_w &= \frac{C_w V_w}{C_w V_w + K_d C_w M_s} \\ &= \frac{V_w}{V_w + K_d M_s} \end{aligned} \quad (11-4)$$

Finally, noting that we frequently refer to the quotient M_s/V_w as the solid-to-water phase ratio r_{sw} (e.g., $\text{kg} \cdot \text{L}^{-1}$) in the environmental compartment of interest, we may describe the fraction of chemical in solution as a simple function of K_d and this ratio:

$$\begin{aligned} f_w &= \frac{1}{1 + (M_s/V_w) K_d} \\ &= \frac{1}{1 + r_{sw} \cdot K_d} \end{aligned} \quad (11-5)$$

Such an expression clearly indicates that for substances exhibiting a great affinity for solids (hence a large value of K_d) or in situations having large amounts of solids per volume of water (large value of r_{sw}), we predict that correspondingly small fractions of the chemical remain dissolved in the water. Note the fraction associated with solids, f_s , must be given by $(1 - f_w)$ since we assume that no other phases are present (e.g., air, other immiscible liquids).

The fraction of the total volume V_{tot} that is not occupied by solids, the so-called porosity ϕ , is often used instead of r_{sw} to characterize the solid-water phase ratio in a given system. In the absence of any gas phase (as is the case in water-saturated soil and usually in sediments and the open water column), ϕ is equal to

$$\phi = \frac{V_w}{V_{tot}} = \frac{V_w}{V_w + V_s} \quad (11-6)$$

where V_s , the volume occupied by particles, can be expressed by M_s/ρ_s , (where ρ_s is the density of the solids). Thus

$$\phi = \frac{V_w}{V_w + M_s/\rho_s} = \frac{1}{1 + r_{sw}/\rho_s} \quad (11-7)$$

Solving for r_{sw} yields the corresponding relation

$$r_{sw} = \rho_s \frac{1 - \phi}{\phi} \quad (11-8)$$

It is a matter of convenience whether r_{sw} or ϕ is used.

The application of such solution- versus solid-associated speciation information may be illustrated by considering an organic chemical, say 1,4-dimethylbenzene (DMB), in a lake and in flowing groundwater. In the lake, the solid-water ratio is given by the suspended solids concentration (since $V_w \approx V_{tot}$), which is typically near $10^{-6} \text{ kg} \cdot \text{L}^{-1}$. From experience we may know that the K_d value for DMB in this case is $1 \text{ L} \cdot \text{kg}^{-1}$; therefore we can see that virtually all of this compound is in the dissolved form in the lake:

$$f_w = \frac{1}{1 + 10^{-6} \cdot 1} \approx 1$$

In the groundwater situation, ρ_s for aquifer solids is about $2.5 \text{ kg} \cdot \text{L}^{-1}$ (e.g., quartz density is 2.65); ϕ is often between 0.2 and 0.4. If our particular groundwater situation has ϕ of 0.2, r_{sw} is $10 \text{ kg} \cdot \text{L}^{-1}$. Hence, we predict that the fraction of DMB in solution, assuming again a K_d of $1 \text{ L} \cdot \text{kg}^{-1}$, is drastically lower than in the lake:

$$f_w = \frac{1}{1 + 10.1} \approx 0.09$$

So we deduce that only one DMB molecule out of 11 will be in the moving groundwater at any instant (Fig. 11.4). This result has implications for the fate of the DMB in that subsurface environment. If DMB sorptive exchange between the aquifer solids and the water is fast relative to the groundwater flow and if sorption is reversible, we can conclude that the whole population of DMB molecules moves at one eleventh the rate of the water. The phenomenon of diminished transport speed relative to the water seepage velocity is referred to as retardation; and it is quantified using a retardation factor which is simply f_w^{-1} .

Many situations require us to know something about the distribution of a chemical between a solution and solids. Our task then is to see how we can get K_d values suited for the cases that concern us. As we will see, these K_d values are determined by the structures of the sorbates as well as the composition of the aqueous phase and the sorbents.



Figure 11.4 Illustration of the retardation of 1,4-dimethylbenzene (DMB) transport in groundwater due to: (1) reversible sorptive exchange between water and solids, and (2) limiting transport of DMB to that fraction remaining in the flowing water. As dissolved molecules move ahead they become sorbed and stopped, while molecules sorbed at the rear return to the water and catch up. Thus, overall transport of DMB is slower than that of the water itself.

11.3 THE COMPLEX NATURE OF K_d 's

The prediction of K_d for any particular combination of organic chemical and solids in the environment can be difficult, but fortunately many situations appear reducible to fairly simple limiting cases. We begin by emphasizing that the way we defined K_d means that we may have lumped together many chemical species in each phase. For example, referring again to Figure 11.2, we recognize that the total concentration of 4-chloroaniline in the sorbed phase combines the contributions of molecules in many different sorbed forms. Even the solution in this case contains both a neutral and a charged species of this chemical. Thus the distribution ratio for this case would have

to be written

$$K_d = \frac{C_{om} \cdot f_{om} + C_{min} \cdot A + C_{ie} \cdot \sigma_{ie} \cdot A + C_{rxn} \cdot \sigma_{rxn} \cdot A}{C_{w,neut} + C_{w,ion}} \quad (11-9)$$

where

C_{om} is the concentration of sorbate associated with the natural organic matter ($\text{mol} \cdot \text{kg}^{-1} \text{om}$),

f_{om} is the weight fraction of solid which is natural organic matter ($\text{kg om} \cdot \text{kg}^{-1} \text{solid}$),

C_{min} is the concentration of sorbate associated with the mineral surface ($\text{mol} \cdot \text{m}^{-2}$),

A is the area of mineral surface per mass of solid [$\text{m}^2 \cdot \text{kg}^{-1} \text{solid}$],

C_{ie} is the concentration of ionized sorbate drawn toward positions of opposite charge on the solid surface ($\text{mol} \cdot \text{mol}^{-1} \text{surface charges}$),

σ_{ie} is the net concentration of suitably charged sites on the solid surface ($\text{mol surface charges} \cdot \text{m}^{-2}$),

C_{rxn} is the concentration of sorbate bonded in a reversible reaction to the solid ($\text{mol} \cdot \text{mol}^{-1} \text{rxn sites}$),

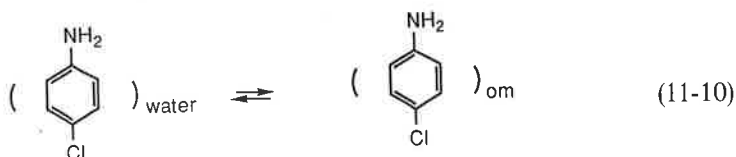
σ_{rxn} is the concentration of reactive sites on the solid surface ($\text{mol rxn sites} \cdot \text{m}^{-2}$),

$C_{w,neut}$ is the concentration of uncharged chemical in solution ($\text{mol} \cdot \text{L}^{-1}$), and

$C_{w,ion}$ is the concentration of the charged chemical in solution ($\text{mol} \cdot \text{L}^{-1}$).

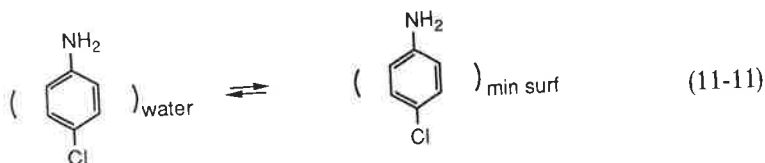
It is possible that some of the terms in Eq. 11-9 also deserve further subdivision. For example, $C_{min} \cdot A$ may reflect a linear combination of the interactions of several mineral surfaces present in a particular soil or sediment with a single sorbate. Thus, a soil consisting of montmorillonite, kaolinite, iron oxide, and quartz mineral components may actually have $C_{min} \cdot A = C_{mont} \cdot a \cdot A + C_{kao} \cdot b \cdot A + C_{iron\ ox} \cdot c \cdot A + C_{quartz} \cdot d \cdot A$ where the parameters a, b, c , and d are the area fractions exhibited by each mineral type. Similarly, $C_{rxn} \cdot \sigma_{rxn} \cdot A$ may reflect bonding to several different kinds of moieties, each with its own reactivity with the sorbate (e.g., chloroaniline). For now, we will work from the simplified expression which is Eq. 11-9, primarily because there are little data available allowing rational subdivisions of soil or sediment differentially sorbing organic chemicals beyond that reflected in this equation.

It is very important to realize that only particular combinations of species in the numerator and denominator of complex K_d expressions like that of Eq. 11-9 are involved in any one exchange process. For example, in the case of 4-chloroaniline

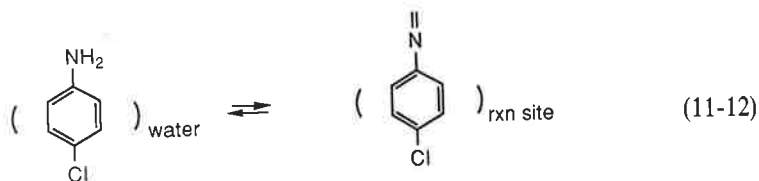


reflects the molecular interchange between the uncharged chloroaniline species

dissolved in water and the species in the particulate natural organic phase with the same molecular structure. Similarly, the combination

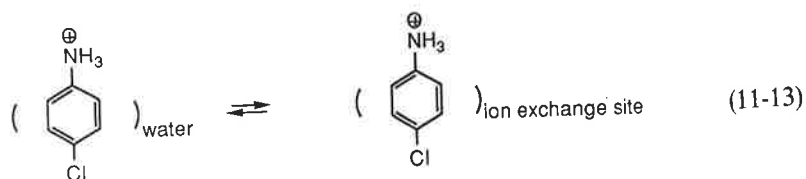


would indicate the exchange of uncharged chloroaniline molecules from aqueous solution to the available mineral surfaces. Each of these exchanges is characterized by a unique free energy difference reflecting the equilibria shown as Eqs. 11-10 and 11-11. Similarly, the exchange of



should be considered if it is the neutral sorbate which can react with components of the solid. Note that such specific binding to a particular solid phase moiety may prevent rapid desorption, and therefore such sorbate-solid associations may cause part or all of the sorption process to appear irreversible on some timescale of interest.

So far we have considered sorptive interactions in which the neutral chloroaniline species was involved. In contrast, it is the charged chloroaniline species that is important in the ion exchange process:



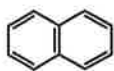
Again, we emphasize this solution-solid exchange has to be described using the appropriate equilibrium expression relating corresponding species in each phase. The influence of each sorption mechanism on the overall K_d is weighted by the availability of the respective sorbent property (i.e., f_{om} , A , σ_{ie} , σ_{rxn} , or A) in the total solid. By combining information on the individual equilibria (e.g., Eqs. 11-10 through Eq. 11-13) with these sorbent properties, we can develop versions of the complex K_d expression (Eq. 11-9) which take into account the structure of the chemical we are considering. In the following sections, we discuss these individual equilibrium relationships.

11.4 SORPTION OF NEUTRAL ORGANIC CHEMICALS TO SOILS AND SEDIMENTS

Role of the Natural Organic Matter

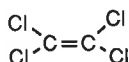
We begin by treating the case of *neutral organic chemicals* distributing themselves between an aqueous solution and natural solids. Our major emphasis involves non-polar compounds constructed primarily from carbon, hydrogen and halogen atoms such as those shown below:

Naphthalene



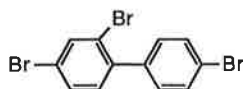
Isooctane

Tetrachloroethylene

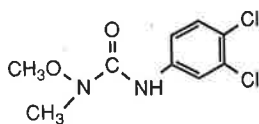


Freon-12

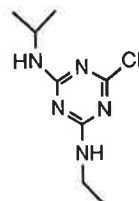
2,4,4'-Tribromobiphenyl



However, much of the following treatment also applies for more polar, but still neutral, chemicals like



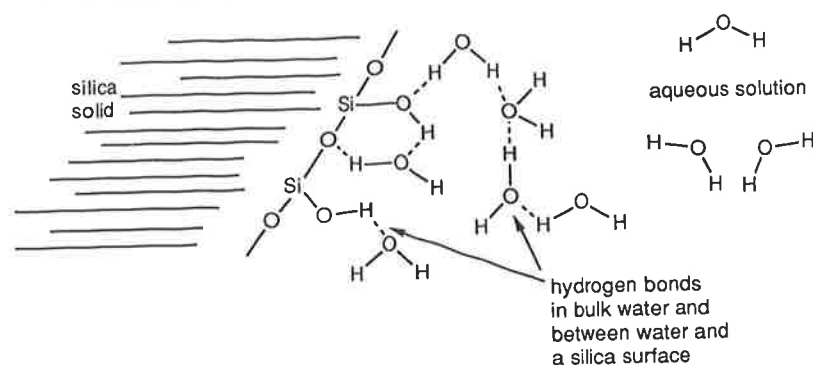
Linuron
(a phenyl urea herbicide)



Atrazine
(a chloro-s-triazine herbicide)

As we have seen in discussing the aqueous solubilities of nonpolar compounds (Chapter 5), these molecules do not "enthusiastically" dissolve in water. This incompatibility principally arises because water molecules change their overall H-bonding to their surroundings when they are forced to interface with such nonpolar solutes or nonpolar structural subunits of compounds like linuron and atrazine.

In like manner, most natural minerals are polar and expose a combination of hydroxy- and oxy-moieties to their exterior. Naturally, then, these polar surfaces strongly favor interactions which allow them to form hydrogen bonds—such as with liquid water:



As a result, replacing the water molecules at such a mineral surface by nonpolar organic compounds is unfavorable from an energetic point of view, despite the sorption-favoring activity coefficients of these solutes in the water.

On the other hand, penetration of neutral organic chemicals into any natural organic matter included in the solid phase does not require displacement of tightly bound water molecules. This solid organic phase material may include recognizable biopolymers like proteins, lignin, and cellulose, but also a menagerie of macromolecules from the partial degradation and crosslinking of organic residues remaining from organisms or photochemical reactions. Naturally, the structure of such altered materials will depend on the ingredients supplied by the particular organisms living in or near the water or soil and will tend to be somewhat randomized depending on what particular substituents have been altered and where crosslinking has happened to occur. For example, soil scientists (Schnitzer and Khan, 1972; Stevenson, 1976) have deduced that the recalcitrant remains of woody terrestrial plants make up a major portion of the natural organic matter in soils. Such materials also make up an important fraction of organic matter suspended in freshwaters (Liao et al., 1982). Similarly, marine chemists believe that the natural organic matter, suspended in the oceans at sites far from land, consists of altered biomolecules such as amino acids, sugars, and triglycerides that have been linked together (Hedges, 1977; Stuermer and Payne, 1976; Harvey et al., 1983). At intermediate locales, such as large lakes and estuaries, the natural organic material in sediments and suspended in water appears to derive from a variable mixture of terrestrial organism and planktonic organism remains (Hedges and Parker, 1976; Sigleo et al., 1982; Hedges et al., 1984; Thurman, 1985). These altered complex organic substances are typically referred to as *humic substances* if they are soluble or extractable in aqueous base, and *humic* or *kerogen* if they are not. The humic substances are further subdivided into *fulvic acids* if they are soluble in both acidic and basic solutions and *humic acids* if they are not soluble in acidic conditions but are soluble at high pHs. Such materials are predominantly made of carbon (about 40–50% by weight), but some have nearly as many oxygens as carbons included in their structures (Table 11.1). Thus, they are not as polar as water, especially since they can only be involved in H-bonding at limited points on their structures (e.g., carboxy, phenoxy, hydroxy, and carbonyl substituents); but they are not as nonpolar as hydrocarbons or chlorinated hydrocarbons either, since they

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TABLE 11.1 Properties of Natural Organic Matter Relevant to Sorption

	Mole Ratio				Moles H-bonding Substituents per kg				Molecular Mass Range (amu)	Reference
	C	H	N	O	ether	keto	hydroxy	carboxy		
Proteins	10	15	4	2					$1 \times 10^4 - 1 \times 10^5$ (cytochrome c to serum γ -globulin)	5
Cellulose (linear polymer)	10	16	0	8	1.2	0	1.9	0	$3 \times 10^5 - 4 \times 10^6$ (cotton)	2
Lignin	10	11	0.1	3						2
Fulvic acids	10	12	0.2	6		2	9	6	1×10^3	3
Dissolved (river)	10	8	0.1	7	0.1	3.1	6.9	9.1		1
Soils										
Humic acids	10	11	0.3	6				4.3	$2 \times 10^3 - 5 \times 10^3$	3
Dissolved (river)	10	13	0.9	5						4
Sedimentary (lake)	10	12	0.6	4	0.3	4.4	4.9	4.5	$1 \times 10^3 - 2 \times 10^5$	1, 4
Soils	10	19	0.5	11						2
Humins										

References: 1. Khan, 1980. 2. Garbarini and Lion, 1986. 3. Thurman, 1985. 4. Schnitzer and Khan, 1972. 5. Oser, 1965.

do have oxygens and a few nitrogens in their structures. Such natural organic matter occurs in a very broad spectrum of molecular sizes from the smallest fulvic acids of about 1000 amu (corresponding to spheres of about 2 nm diameter) to the huge complexes of solid kerogen. The important point is that when these natural organic constituents are associated with particles (and even when they remain suspended as nonsettling particles called colloids in aqueous solution), they offer a relatively nonpolar environment into which a hydrophobic compound may escape without undue competition with water.

In light of this discussion, we may not be too surprised to find that nonreactive, neutral chemicals show greater solid-water distribution ratios for soils or sediments that contain high amounts of natural organic matter, as illustrated for pyrene in Figure 11.5. Additionally, we see in this figure that when f_{om} approaches zero, K_d (pyrene) is very small. (Note: f_{om} is often determined by measurement of organic carbon (oc); as a result, it is often discussed using a parameter called f_{oc} , or fraction organic carbon, with units $\text{kg oc} \cdot \text{kg}^{-1}$ solid. As shown by the materials listed in Table 11.1, natural organic matter is typically made up of about half carbon, so f_{om} approximately equals $2 \cdot f_{oc}$.)

Consequently, we conclude that we only need to consider sorption of neutral nonpolar organic compounds to the natural organic matter as long as f_{om} is "significant". A more precise definition of "significant" will emerge below as we consider competing sorption mechanisms. For now, we realize that in this type of case, $C_s \approx C_{om} \cdot f_{om}$. Since chemicals like pyrene cannot ionize, C_w is equal to $C_{w,neut}$. Thus the composite

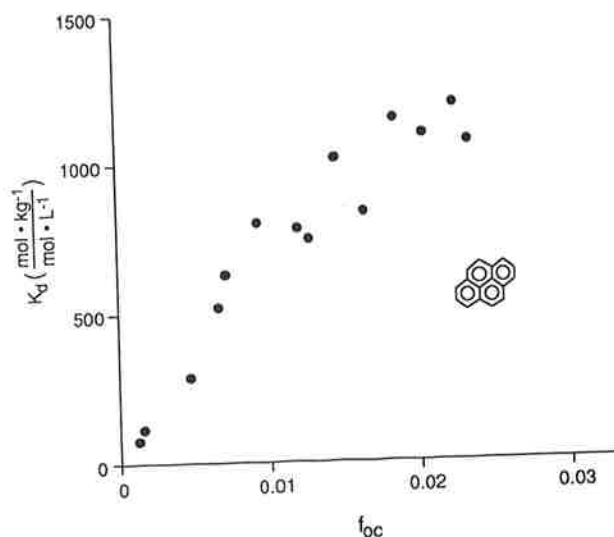


Figure 11.5 Observed increase in solid-water distribution ratios for a hydrophobic compound, pyrene, as a function of the organic matter content of the solid (measured as organic carbon, $f_{oc} \approx 1/2 f_{om}$) in a variety of soils and sediments. Data from Means et al. (1980).

K_d (Eq. 11-9) simplifies to

$$K_d = \frac{C_{om} \cdot f_{om}}{C_{w,neut}} \quad (11-14)$$

The Organic Matter—Water Partition Coefficient, K_{om}

To ascertain what controls the ratio of C_{om} to $C_{w,neut}$ for various situations, we consider briefly the molecular environment of a neutral organic molecule sorbed by natural organic matter. We picture this natural organic material to exist in large part as organic chains coiled into globular units, much like globular proteins, and to occur in somewhat isolated patches coating mineral solids (Fig. 11.6). Such coiling is brought about because the natural organic matter minimizes the hydrophobic surface area it exposes to the aqueous solution. Because of the "porous" nature of such flexible macromolecules, nonpolar sorbates can physically penetrate between the chains and find themselves "dissolved" in the nonaqueous medium (Fig. 11.6). Note that such sorbent associations are not limited to the interfacial area where the water solvent contacts the natural organic sorbent. Indeed, since the sorbate goes *into* the "volume" of the sorbent, this process may be referred to as an *absorption* (from Latin, *ab*, away from, and *sorbere*, to suck). The entry of nonpolar sorbates into the natural organic matter amounts to mixing these components as in solutions.

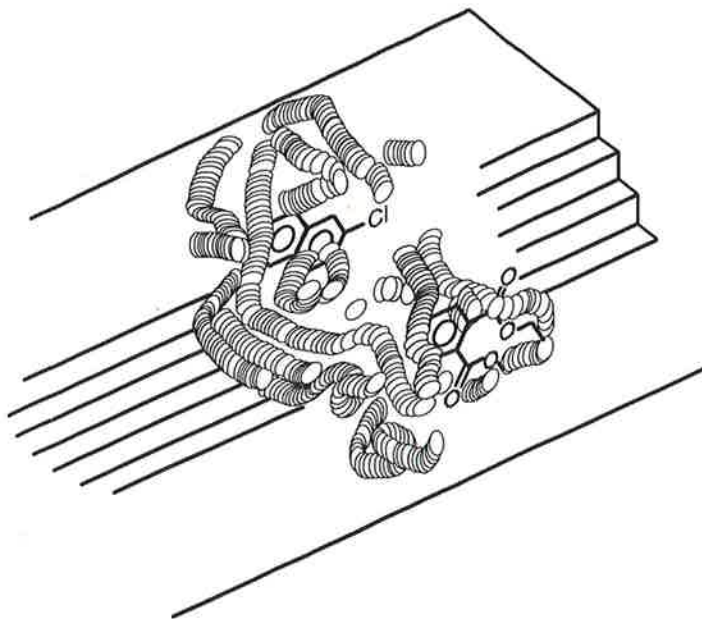


Figure 11.6 Conceptualization of nonpolar organic sorbates (here, 2-chloronaphthalene and diethylphthalate) associated with natural organic matter in a solid phase.

Thus we can imagine the organic sorbate is distributing itself between two immiscible solutions, and we may define a partition coefficient which reflects the ratio of these concentrations:

$$K_{om} = \frac{C_{om} \text{ (mol} \cdot \text{kg}_{om}^{-1})}{C_{w,neut} \text{ (mol} \cdot \text{L}_{water}^{-1})} \quad (11-15)$$

which is analogous to what we defined for organic solvent-water partitioning (Eq. 7-1). In defining K_{om} this way, we have led to a new expression for the solid-water distribution ratio of such neutral, nonpolar chemicals:

$$K_d = \frac{f_{om} \cdot C_{om}}{C_{w,neut}} \quad (11-14)$$

$$= f_{om} \cdot K_{om} \quad (11-16)$$

This formulation will prove to be very convenient because it is broken into two parts: f_{om} , which is a property of the soil or sediment sorbent, and K_{om} , which is primarily a characteristic of the organic chemical sorbate.

Given our conceptualization of hydrophobic neutral chemical absorption as two solutions competing for the sorbate, we can deduce several important results. First, considering C_{om} and $C_{w,neut}$ to be solution concentrations, we may rewrite the equilibrium partition coefficient expression (Eq. 11-15):

$$K_{om} = \frac{x_{om} \cdot \bar{V}_{om}^{-1} \cdot \rho_{om}^{-1}}{x_w \cdot \bar{V}_w^{-1}} \quad (11-17)$$

where x_{om} (mol sorbate \cdot mol⁻¹ om) and x_w (mol sorbate \cdot mol⁻¹ water) refer to the mole fraction concentrations in the organic matter and aqueous solutions, respectively; \bar{V}_{om} (L om \cdot mol⁻¹ om) and \bar{V}_w (L water \cdot mol⁻¹ water) are the molar volumes of the two phases, and ρ_{om} (kg om \cdot L⁻¹ om) is the organic matter density. Choosing the pure liquid of the sorbate to serve as the reference state, we may use the relation $x = \gamma^{-1}$ to rewrite Eq. 11-17:

$$K_{om} = \frac{\gamma_w \cdot \bar{V}_w}{\gamma_{om} \cdot \bar{V}_{om} \cdot \rho_{om}} \quad (11-18)$$

where γ_{om} is the activity coefficient reflecting the incompatibility of the sorbate associated with the natural organic matter as compared to in solution with a liquid of itself. Again, this result is analogous to what we had before for partitioning between organic solvents and water (see Eq. 7-4).

Now, for a given chemical sorbate and a particular soil or sediment, all the terms on the right-hand side of Eq. 11-18 may be virtually constant for all concentrations of the hydrophobic sorbate in water. As we saw before, γ_w is practically independent of C_w for neutral nonpolar compounds (see Section 6.2); and since \bar{V}_w , \bar{V}_{om} , and ρ_{om} are properties of the solution and solid phase which are generally unaffected by the

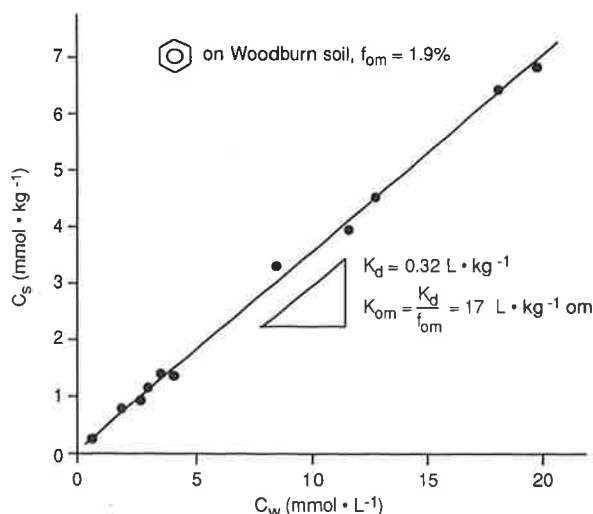


Figure 11.7 Linear variation of sorbed benzene concentration C_s with aqueous benzene concentration C_w up to 85% of benzene's solubility in water. Data from Chiou et al. (1983).

presence of submillimolar levels of neutral nonpolar compounds, these inputs to Eq. 11-18 may reasonably be presumed constant. Finally, the activity coefficient of a sorbate in natural organic matter may not be too much above 1 if this material can be as accommodating as a solvent like octanol (recall Table 7.1); and therefore it should not change much if more and more organic sorbate is mixed into this particular phase. Thus, one can expect K_{om} to remain constant for a particular sorbate-sorbent combination at all concentrations of the compound in the water. This means that the solid-water distribution ratio K_d must also remain invariant (i.e., a linear isotherm), since the product $f_{om} \cdot K_{om}$ does not change. This is seen experimentally, as shown in Figure 11.7 for benzene absorption on a soil. Here we see the concentration of benzene associated with this particular soil increased linearly as the levels of this compound in the water were increased. The slope of this graph yields the solid-water distribution ratio for this case:

$$K_d(\text{benzene, Woodburn soil}) = \frac{C_s}{C_w} = 0.32 \frac{\text{mol} \cdot \text{kg}^{-1} \text{ soil}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \quad (11-19)$$

And realizing that the natural organic matter of the soil ($f_{om} = 0.019$) was predominately responsible for benzene sorption, we may also calculate

$$\begin{aligned} K_{om}(\text{benzene}) &= \frac{K_d(\text{benzene, Woodburn soil})}{f_{om}(\text{Woodburn soil})} \\ &= 17 \frac{\text{mol} \cdot \text{kg}^{-1} \text{ om}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \end{aligned} \quad (11-20)$$

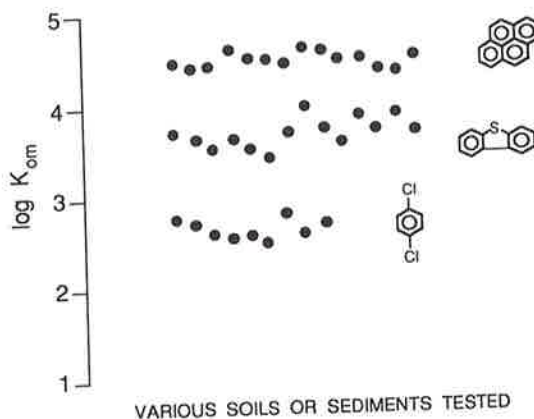


Figure 11.8 Similarity of $\log K_{om}$ values observed for particular nonpolar organic chemicals absorbing to a wide variety of soils and sediments. Data from Means et al. (1980), Hassett et al. (1980), Schwarzenbach and Westall (1981), and Chiou et al. (1983).

When one examines the K_{om} values for a single neutral nonpolar chemical sorbing to a variety of soils and sediments, one typically finds almost the same K_{om} result. Figure 11.8 shows such constancy of K_{om} for three chemicals: 1,4-dichlorobenzene, dibenzothiophene, and pyrene, sorbing to many soils and sediments. This near constancy of K_{om} values for a nonpolar organic chemical can be interpreted by considering Eq. 11-18. First, it is obvious that the numerator, $\gamma_w \cdot \bar{V}_w$, does not change for different sorbents. If the composition of natural organic matter does not vary much from the point of view of acting as a solvent for neutral nonpolar chemicals, then for a variety of sediments and soils, the product $\gamma_{om} \cdot \bar{V}_{om} \cdot \rho_{om}$ may also be similar. Much of the variability shown in Figure 11.8 is due to substantially different analytical techniques used by various investigators, but some is probably caused by differences in the polarity of the natural organic matter investigated (Garbarini and Lion, 1986; Chiou et al., 1987; Gauthier et al., 1987). But even including such variability, for any one chemical it seems $\log K_{om}$ is a constant within $\pm 0.3 \log K_{om}$ units (\pm a factor of 2 in K_{om}).

Linear Free Energy Relationships to Estimate K_{om} 's Now we may consider what factor(s) governs the magnitude of the K_{om} for a particular neutral nonpolar sorbate. For a series of compounds absorbing into the natural organic matter of a single soil or sediment (hence \bar{V}_w , \bar{V}_{om} and ρ_{om} in Eq. 11-18 held constant), we need to evaluate the sizes of their γ_w 's and γ_{om} 's. This is very similar to the situation we discussed before regarding organic solvent-water partitioning (Chapter 7). Since the organic sorbates are much more similar to the natural organic matter than to the water in terms of polarity and ability to interact with their surroundings via intermolecular attractions, we expect the γ_w 's will be much larger than γ_{om} 's, and that the γ_{om} 's will not be much greater than 1. Once again, this is analogous to what we encountered

in the case of organic chemical partitioning between octanol and water (Table 7.1). Since the γ_{om} 's are near 1, they will not vary much from organic chemical to chemical; in contrast, we know that various neutral organic chemicals exhibit γ_w 's that vary by orders of magnitude (see Chapter 5). Consequently, differences, in K_{om} from chemical to chemical primarily arise from corresponding differences in their γ_w 's.

A major result of realizing the strong relationship of K_{om} 's and γ_w 's for a series of organic sorbates is that we deduce that the free energy driving this absorption is determined largely by the excess free energy of aqueous solution (i.e., $\Delta G_{\text{sorption to om}} \sim \Delta G_s^e$). This situation is therefore well suited to a free energy relationship between $\Delta G_{\text{absorption}}$ and ΔG_s^e . Indeed, plots of $\log K_{om}$ ($= -\Delta G_{\text{absorption}}/2.303 RT$) versus $\log C_w^{\text{sat}}(l, L)$ ($= -\Delta G_s^e/2.303 RT - \log \bar{V}_w$) for various sets of organic compounds show strong inverse correlations of the form (Table 11.2)

$$\log K_{om} = -a \cdot \log C_w^{\text{sat}}(l, L) + b \quad (11-21)$$

where K_{om} is given in units of $(\text{mol} \cdot \text{kg}^{-1} \text{ om} / \text{mol} \cdot \text{L}^{-1} \text{ water})$ and C_w^{sat} has units of $(\text{mol} \cdot \text{L}^{-1} \text{ water})$. For different sets of sorbates, different values of the coefficients a and b are seen and this undoubtedly reflects systematic variations in the compatibility of compound classes with the natural organic matter. Nonetheless, an overall strong inverse correlation of $\log K_{om}$ with $\log C_w^{\text{sat}}(l, L)$ exists as shown in Figure 11.9.

Since K_{om} and $C_w^{\text{sat}}(l, L)$ properties of sorbates are related, it follows that any other

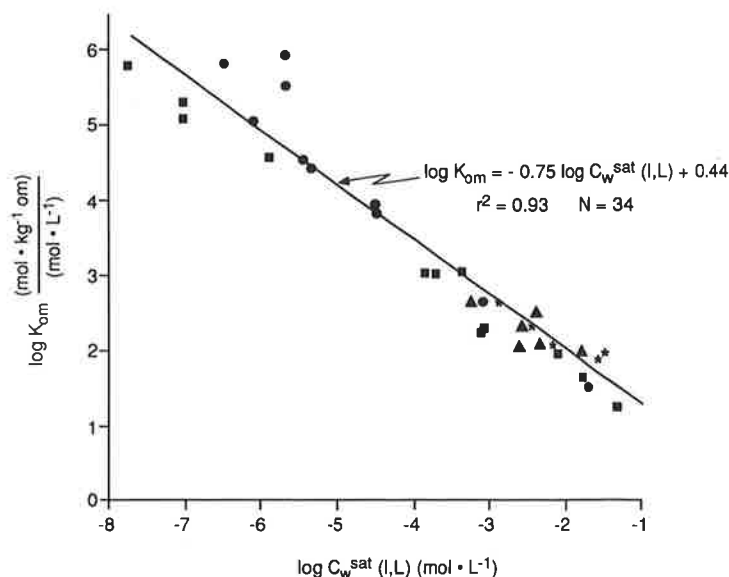


Figure 11.9 Inverse relationship of $\log K_{om}$ and \log (liquid) aqueous solubility of neutral organic compounds: (●) aromatic hydrocarbons, (■) chlorinated hydrocarbons, (▲) chloro-S-triazines, and (*) phenyl ureas (data compiled by Karickhoff, 1981). See Table 11.2 for correlations for individual compound classes.

TABLE 11.2 LFERs Between $\log K_{om}$ and $\log C_w^{sat}(l, L)$ or $\log K_{ow}^a$

	$a =$	$\log K_{om} = -a \cdot \log C_w^{sat}(l, L) + b$ ($L \cdot kg^{-1} om$)($mol \cdot L^{-1}$)	$b =$	(r^2)	Compound Class
Eq. 11-21a	0.93		-0.17	(0.92)	Aromatic hydrocarbons
Eq. 11-21b	0.70		+ 0.35	(0.99)	Chlorinated hydrocarbons
Eq. 11-21c	0.41		+ 1.20	(0.54)	Chloro-S-triazines
Eq. 11-21d	0.56		+ 0.97	(0.94)	Phenyl ureas
	$c =$	$\log K_{om} = c \cdot \log K_{ow} + d$ ($L \cdot kg^{-1} om$)($L_{water} \cdot L_{octanol}^{-1}$)	$d =$		
Eq. 11-22a	1.01		-0.72	(0.99)	Aromatic hydrocarbons
Eq. 11-22b	0.88		-0.27	(0.97)	Chlorinated hydrocarbons
Eq. 11-22c	0.37		+ 1.15	(0.93)	Chloro-S-triazines
Eq. 11-22d	1.12		+ 0.15	(0.93)	Phenyl ureas
Eq. 11-22e	0.81		-0.25	(0.98)	Chlorophenols

^aData from Karickhoff, 1981 and Schellenberg et al., 1984.

chemical property which is related to $C_w^{\text{sat}}(l, L)$ must also correlate with K_{om} . For example, $\log K_{\text{om}}$ should be directly related to $\log K_{\text{ow}}$ [inversely proportional to $\log C_w^{\text{sat}}(l, L)$, see Chapter 7]. Table 11.2 also shows the values of the slope and intercept of relationships for compound classes of the form

$$\log K_{\text{om}} \left[\frac{\text{mol} \cdot \text{kg}^{-1} \text{ om}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \right] = c \cdot \log K_{\text{ow}} \left[\frac{\text{mol} \cdot \text{L}^{-1} \text{ octanol}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \right] + d \quad (11-22)$$

Again, the values of this equation's coefficients vary between compound classes, but the overall trend is strong (Fig. 11.10).

Such linear free-energy relationships (Eqs. 11-21 and 11-22) provide one of the best means with which we can use well-known physical chemical properties of neutral chemicals [e.g., $C_w^{\text{sat}}(l, L)$ and K_{ow}] to estimate the magnitude of K_{om} for a compound of interest. Obviously, one obtains a somewhat more accurate estimate if one uses a correlation equation based on a set of chemicals from the sorbate's own compound class; however, without this kind of information, a reasonable K_{om} estimate can be obtained from expressions averaging results from many compound classes (like those illustrated in Figs. 11.9 and 11.10):

$$\log K_{\text{om}} \left[\frac{\text{mol} \cdot \text{kg}^{-1} \text{ om}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \right] \simeq -0.75 \log C_w^{\text{sat}}(l, L) (\text{mol} \cdot \text{L}^{-1} \text{ water}) + 0.44 \quad (11-23)$$

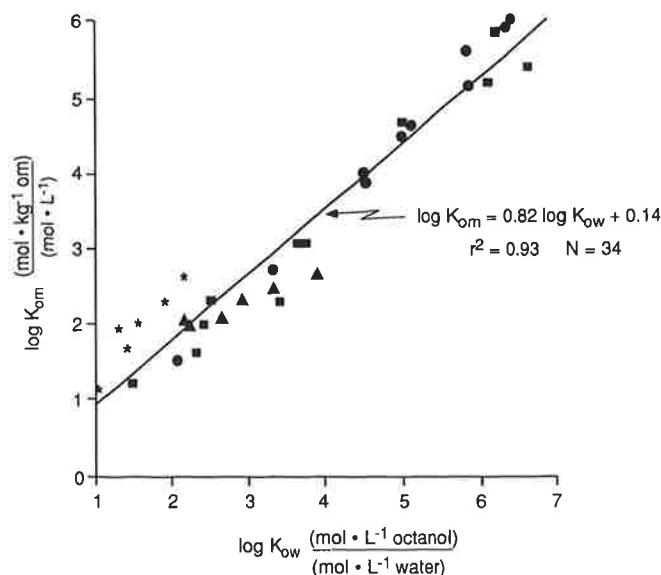


Figure 11.10 Relationship of $\log K_{\text{om}}$ and $\log K_{\text{ow}}$ for a series of neutral organic compounds: (●) aromatic hydrocarbons, (■) chlorinated hydrocarbons, (▲) chloro-S-triazines, and (*) phenyl ureas (data compiled by Karickhoff, 1981). See Table 11.2 for correlations of each compound class.

or

$$\log K_{om} \left[\frac{\text{mol} \cdot \text{kg}^{-1} \text{ om}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \right] \approx +0.82 \log K_{ow} \left[\frac{\text{mol} \cdot \text{L}^{-1} \text{ octanol}}{\text{mol} \cdot \text{L}^{-1} \text{ water}} \right] + 0.14 \quad (11-24)$$

Reversibility and Competitive Effects of Neutral Compound Sorption to Natural Organic Matter Our image of neutral chemical interactions with the natural organic matter of particles suggests that such sorption must be *reversible*. We see that the only "bonds" that are made between the sorbate and the natural organic sorbent are through relatively weak intermolecular attractions. Thus, to desorb these nonpolar chemicals, only small activation energies are needed to separate these compounds from their points of solid attachment. This reversibility has been demonstrated experimentally for nonpolar compounds like polycyclic aromatic hydrocarbons and nonpolar insecticides (Karickhoff et al., 1979), PCB congeners (Gschwend and Wu, 1985), and solvents like tetrachloroethylene and toluene (Garbarini and Lion, 1985). Additionally, many nonpolar chemicals can partition between water and the available volume of natural organic matter at the same time and without getting in each others' way (Karickhoff et al., 1979; Chiou et al., 1983). We refer to this as *noncompetitive* sorption. As was the case for organic solvent-water partitioning, this implies that so little nonpolar chemical enters the organic phase that the overall properties of the natural organic matter do not change and the resultant intermolecular interactions within the medium remain essentially constant.

Effect of Temperature on K_{om} Since we envision neutral compound absorption to be like a solvent-water partitioning process, we can immediately deduce the likely effect of conditions such as temperature on K_{om} . First, as we recall from our discussions of aqueous solubility, over a narrow temperature range, the logarithm of a chemical's aqueous activity coefficient varies according to (see Section 5.4)

$$\ln \gamma_w = \frac{\Delta H_s^e}{RT} + \text{constant} \quad (11-25)$$

Thus, the variation in γ_w with temperature will depend on the magnitude of ΔH_s^e . Typically, small nonpolar solutes like benzene exhibit small values of ΔH_s^e , but within any one family of compounds (e.g., PAHs or alcohols), we saw that ΔH_s^e steadily increased as the nonpolar molecular surface area of contact with the water solvent increased. A similar expression should apply for γ_{om} .

$$\ln \gamma_{om} = \frac{\Delta H_{s,om}^e}{RT} + \text{constant} \quad (11-26)$$

where $\Delta H_{s,om}^e$ is the excess enthalpy of the sorbate's mixing with natural organic matter. If the natural organic matter can approximately mimic the van der Waals attractions over the molecular surface that the sorbate enjoyed in a pure liquid of itself, then the change in enthalpy of dissolution into natural matter from the pure

organic liquid will be quite small. This result, in turn, implies that γ_{om} is not particularly sensitive to temperature.

Since \bar{V}_w and \bar{V}_{om} vary only slightly with temperature, the effect of temperature on K_{om} values will chiefly arise from its impact on γ_w . Although very little data is available to check this conclusion, the literature does support it. First, Chiou et al. (1979) reported very small heats of absorption for organic chemicals frequently used as solvents, consistent with their small heats of solution in water. Also, Wu and Gschwend (1986) observed ΔH_{abs} of 1,2,3,4-tetrachlorobenzene to be about $-15 \text{ kJ} \cdot \text{mol}^{-1}$. Although the heat of solution of this compound has not been directly measured, it can be estimated using Eq. 5-18, the known (liquid) solubility of this compound ($10^{-4.20} \text{ M}$ or $1.14 \times 10^{-6} \text{ mol fraction}$), and an estimate of ΔS_s° of $-56 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ (see Table 5-3). Thus,

$$\begin{aligned}\Delta H_s^\circ &\simeq -RT \ln x_w + T \Delta S_s^\circ \\ &= -(8.31 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1})(293 \text{ K})(\ln 1.14 \times 10^{-6}) \\ &\quad + (293 \text{ K})(-56 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}) \\ &= 33 \text{ kJ} \cdot \text{mol}^{-1} - 16 \text{ kJ} \cdot \text{mol}^{-1} \\ &= +17 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}\tag{11-27}$$

For the process removing the solute from the sorbent, this enthalpy would be negative in approximate agreement with the observed enthalpy of sorption ($-15 \text{ kJ} \cdot \text{mol}^{-1}$). Consequently, it appears reasonable to expect K_{om} to vary in an equal, but opposite, manner as the neutral chemical's liquid solubility in water. For large nonpolar compounds like pyrene exhibiting $\Delta H_s^\circ \simeq +25 \text{ kJ} \cdot \text{mol}^{-1}$, we then anticipate an *exothermic* $\Delta H_{abs} \approx -25 \text{ kJ} \cdot \text{mol}^{-1}$. Such enthalpy effects imply pyrene's sorption to natural particles should decrease as we increase temperature:

$$\begin{aligned}\frac{K_{om}(T_1 = 293 \text{ K})}{K_{om}(T_2 = 283 \text{ K})} &\simeq \frac{\gamma_w(293 \text{ K})}{\gamma_w(283 \text{ K})} \\ &\simeq \exp \left[\frac{\Delta H_s^\circ}{R} \left(\frac{1}{293} - \frac{1}{283} \right) \right] \\ &\simeq 0.7\end{aligned}\tag{11-28}$$

That is, warming a solid-water suspension by 10°C results in an estimated 30% diminished absorption coefficient as a consequence of correspondingly decreased activity coefficient for pyrene in water.

Effect of Dissolved Salts on K_{om} Since solvated inorganic ions would not be expected to interfere or compete with the penetration of nonpolar organic compounds into natural organic matter, one can reasonably assume that salts affect the values of K_{om} primarily through the γ_w term also. As we saw in Chapter 5, a quantitative description of the impact of dissolved salts on aqueous solubilities (and hence γ_w 's)

was provided by the Setschenow relationship; a transformation of this formula (Eq. 5-22) yields

$$C_{w,salt}^{sat} = C_w^{sat} \cdot 10^{-K^s[salt]} \quad (11-29)$$

Since K_{om} values are predictable from a chemical's $C_w^{sat}(1, L)$, we may substitute Eq. 11-29 into Eq. 11-21 to characterize how K_{om} changes in the presence of dissolved salts:

$$\begin{aligned} \log K_{om,salt} &= -a \cdot \log(C_{w,salt}^{sat}) + b \\ &= -a \cdot \log(C_w^{sat} \cdot 10^{-K^s[salt]}) + b \\ &= -a \cdot \log C_w^{sat} - a \cdot (-K^s) \cdot [salt] + b \\ &= \log K_{om} + a \cdot K^s \cdot [salt] \end{aligned} \quad (11-30)$$

where $K_{om,salt}$ is the organic matter-water partition coefficient when the aqueous solution contains dissolved salts. The second term on the right-hand side of Eq. 11-30 quantifies the magnitude of change we expect for individual cases. As we saw in Table 11.2, a values are typically between 0.5 and 1 for various compound classes, and from Table 5.6 we recall K^s was about 0.1–0.4 depending on the chemical of interest. Thus we may expect $\log K_{om,salt}$ in a salty solution like seawater ($[salt] \approx 0.6$ M) to be higher than $\log K_{om}$ by about $\{(0.5 \text{ to } 1) \cdot (0.1 \text{ to } 0.4) \cdot [0.6]\}$ or 0.03–0.24 log units. This amounts to increasing $K_{om,salt}$ over K_{om} by only several percent for relatively small and polar neutral organic compounds (i.e., a nearer to 0.5 and K^s nearer to 0.1) and by a factor approaching 2 for large, very nonpolar sorbates (i.e., a close to 1 and K^s around 0.4).

As was the case for the effects of temperature on K_{om} , there is not much data to verify these results. Karickhoff et al. (1979) found that pyrene sorption coefficients increased by 15% in going from pure water to sodium chloride solution concentration of 0.34 M. We may compare the effectiveness of Eq. 11-30 by estimating what we would expect for this case. First, for aromatic hydrocarbons Eq. 11-21a suggests a value of a to be 0.93; from Table 5.6 we see that a suitable value for $K^s(\text{pyrene, NaCl})$ would be 0.29. Thus we may estimate for this case:

$$\begin{aligned} \log K_{om,salt}(\text{pyrene, 0.34 M NaCl}) &= \log K_{om}(\text{pyrene}) \\ &\quad + (0.93)(0.29)(0.34) \\ &= \log K_{om}(\text{pyrene}) + 0.09 \end{aligned} \quad (11-31)$$

This predicts that the organic matter-water partition coefficient of pyrene with 0.34 M NaCl would be about 24% higher than the corresponding case without dissolved salt, a result not too different than that which was observed. This discrepancy (15% observed versus 24% predicted) may indicate other factors are at play, such as salts causing changes in the coiling of the natural organic matter and concomitant changes in its solvency for neutral organic sorbates (i.e., changing γ_{om}). However, the prediction

of Eq. 11-31 looks reasonable to a very good first approximation, and one probably rightly concludes that typical levels of dissolved salts do not cause major changes in K_{om} values.

Influence of Cosolvents on K_{om} Sometimes we may be concerned with the sorption of neutral organic compounds to soils from solutions in which a substantial concentration of organic solvent is also present. This could occur, for example, at a groundwater site where water-miscible liquids like acetone or methanol were codisposed with other organic chemicals. In such a case, the tendency of the organic chemicals to sorb to the soil's organic matter might be changed by the organic cosolvent's effects on γ_{om} and γ_w . The inclusion of substantial amounts of the cosolvent into the soil's natural organic matter would influence γ_{om} , but since these activity coefficients are near 1 to start with, such effects are probably not too big. However, as we discussed in Chapter 5, the presence of cosolvents can greatly change a chemical's aqueous solubility. Using our knowledge of that effect, we are already in a position to estimate the importance of cosolvent to K_{om} values.

First, we recall Eq. 5-32 and convert to a molar basis to describe the influence of a cosolvent on a sorbate's solubility:

$$\log C_{mix}^{sat} = \log C_w^{sat} + \log \frac{\bar{V}_w}{\bar{V}_{mix}} + \frac{0.5 f_c N(\sigma_{t:w} - \sigma_{t:c})(HSA)}{2.303 RT} \quad (11-32)$$

where C_{mix}^{sat} is the solubility in an aqueous solution containing an organic cosolvent ($\text{mol} \cdot \text{L}^{-1}$ mixed solution), \bar{V}_{mix} is the molar volume of the mixed solution ($\text{L mixed solution} \cdot \text{mol}^{-1}$ total solvents), and the other terms remain as defined previously (see Section 5.4).

Using this result in our relationship between K_{om} and C_w^{sat} (Eq. 11-21), we arrive at:

$$\begin{aligned} \log K_{om,mix} &= -a \cdot \log(C_{mix}^{sat}) + b \\ &= -a \cdot \left(\log C_w^{sat} + \log \frac{\bar{V}_w}{\bar{V}_{mix}} + \frac{0.5 f_c N(\sigma_{t:w} - \sigma_{t:c})(HSA)}{2.303 RT} \right) + b \\ &= \log K_{om} - a \cdot \left[\log \frac{\bar{V}_w}{\bar{V}_{mix}} + \frac{0.5 f_c N(\sigma_{t:w} - \sigma_{t:c})(HSA)}{2.303 RT} \right] \end{aligned} \quad (11-33)$$

This equation first suggests that the natural organic matter–water partition coefficients will change because of differences in the solution's molar volume from that of water. Also, the third term on the right-hand side of Eq. 11-33 indicates that the attractiveness of the cosolvent–water mixture for maintaining the sorbate in solution will lower $\log K_{om,mix}$ relative to $\log K_{om}$.

A brief calculation exemplifies the magnitude of these effects. Suppose we were interested in the sorption of anthracene ($HSA = 202 \text{ \AA}^2$) from an aqueous solution containing 10% methanol by volume. First, we could calculate that $\bar{V}_{mix} \approx 0.0185 \text{ L} \cdot \text{mol}^{-1}$ total by assuming the methanol and water mix with no change in total volume. Thus

the term $\log(\bar{V}_w/\bar{V}_{mix})$ is quite small (≈ 0.01). Next, to estimate the importance of the second term in brackets of Eq. 11-33, we apply Eq. 11-33 with $(\sigma_{t:w} - \sigma_{t:c})$ taken as $52 \times 10^{-7} \text{ J/cm}^2$:

$$a \cdot \left(\frac{0.5 f_c N (\sigma_{t:w} - \sigma_{t:c}) (HSA)}{2.303 RT} \right) =$$

$$(0.93) \cdot \frac{0.5 \cdot 0.1 \cdot 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mol}} \cdot \left(52 \times 10^{-7} \frac{\text{J}}{\text{cm}^2} \right) \left(202 \times 10^{-16} \frac{\text{cm}^2}{\text{molecule}} \right)}{2.303 \cdot 8.31 (\text{J/mol} \cdot \text{K}) \cdot 293 \text{ K}}$$

$$= 0.52 \quad (11-34)$$

This result implies that $K_{om,mix}$ (pyrene, 10% methanol) is lower than the corresponding K_{om} (pyrene) by a factor of $10^{-0.52}$ or 0.30. Experiments by Nkedi-Kizza et al. (1985) observed anthracene's K_{om} to decrease by a factor of 0.4 under these conditions. These investigators demonstrated that this approach for estimating the influence of cosolvents on K_{om} appears to work well for cosolvent fractions less than 25%.

Sorption of Neutral Chemicals to Organic Colloids Until now, we have not been concerned about the size of the particles with which the nonpolar chemicals became associated. This factor is generally not critical unless we are interested in sorption kinetics (see Section 11.7) or when we are concerned with separating the particles from suspensions. Such a separation becomes important if we are trying to measure contaminant concentrations in the dissolved versus sorbed phases or if we are interested in predicting how a chemical might be carried by moving water. In these cases, one often finds that the smallest of particles, called *colloids*, are not separable from the water. Thus, chemicals of interest to us would occur in the fluid both as truly dissolved species and as molecules associated with very small particles or macromolecules.

Colloids are microparticles or macromolecules that are small enough to move primarily by Brownian motion, as opposed to gravitational settling, and are large enough to provide a microscopic "environment" into or onto which molecules of interest to us can escape the aqueous solution. This means colloids range from about a few nanometers to around a few micrometers in dimension. Based on this perception, organic colloids in natural waters would include humic substances and proteins, viruses and nonmotile bacteria, and organic coatings on very small inorganic particles (e.g., aluminosilicates, iron oxides).

A variety of approaches have been used to demonstrate that colloidal organic matter may serve to absorb nonpolar organic chemicals much like the organic materials associated with larger soil and sediment particles. For example, Chiou et al. (1986) have shown that the "apparent solubility" of compounds like DDT or PCB congeners is increased in solutions containing humic substances over that seen for pure water alone (Fig. 11.11). The interpretation of these data is that the true aqueous solubility is not affected, but rather the additional nonpolar chemical molecules are associated

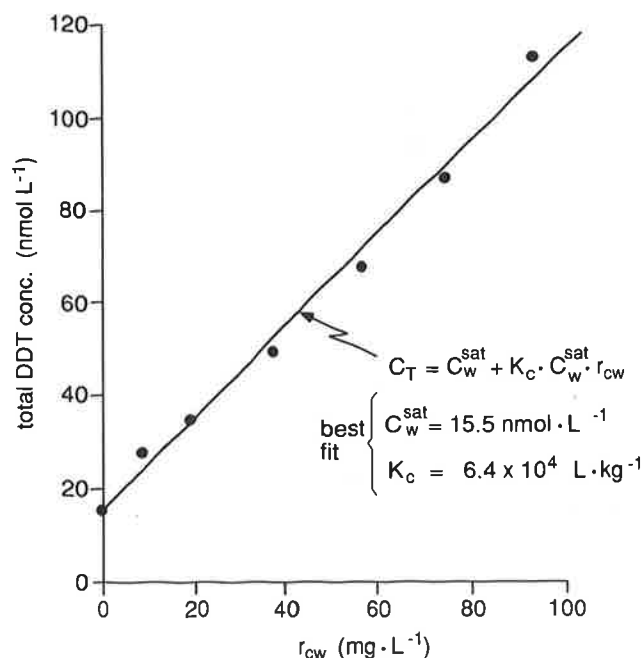


Figure 11.11 Increase in total DDT concentration in aqueous solution as a function of concentration of humic colloids, r_{cw} (data of Chiou et al., 1986). Interpreting the total DDT as a sum of truly dissolved DDT (C_w^{sat}) and DDT bound to colloids ($K_c C_w^{\text{sat}} r_{cw}$) fits the data very well.

with the humic colloids. Similarly, Carter and Suffet (1982) have shown that DDT associates with humic materials retained within dialysis tubing.

Much as we saw before for large sediment and soil particles, the tendency for different organic chemicals to associate with organic colloids is directly related to the aqueous activity coefficient of the chemicals. This should not be too surprising since it is largely the same types of organic matter, whether attached to large mineral grains or dispersed as colloidal suspensions, which are acting as absorbents. Some indications exist which show that there is some decrease in colloidal sorbent effectiveness, especially as the organic matter becomes more polar as reflected in C/O ratios (Chiou et al., 1986; Garbarini and Lion, 1986; Gauthier et al., 1987; Chin and Weber, 1989). Nonetheless, K_{om} values for colloidal organic matter generally appear similar to these reported for larger particulate organic matter.

The association of nonpolar chemicals with colloidal organic matter results in several very important effects on the behavior of those compounds. First, the organic molecules in a colloidal suspension exhibit a tendency to leave the suspension and move into adjacent gaseous phases only in proportion to the truly dissolved fraction of molecules (i.e., proportional to their fugacity). This has been seen in a dynamic system such as that employed by Mackay et al. (1979), where bubbled solutions transmitted the chemicals to the headspace at diminished rates when colloid association

became important. Similarly, Brownawell (1986) observed diminished PCB congener vapor pressures over seawater suspensions of colloids compared to seawater solutions devoid of organic colloids. It is clear from these data that nonpolar chemicals distribute themselves between truly dissolved and colloid-bound states, and that the dissolved species dictate equilibria with other phases. Consequently, when we are interested in colloid-containing solutions that exchange chemicals into the air, we must recognize that the air-water distribution ratio (D_{aw}) describing the concentrations in each phase has the form

$$D_{aw} = \frac{C_a}{C_w + C_c \cdot r_{cw}} \quad (11-35)$$

where C_c is the concentration of chemical associated with colloids per mass of colloid ($\text{mol} \cdot \text{kg}^{-1}$ colloids) and r_{cw} is the mass of colloids per volume of solution ($\text{kg colloids} \cdot \text{L}^{-1}$). If we define a sorption coefficient for the colloids analogous to that for larger particles (Eq. 11-1),

$$K_c = \frac{C_c}{C_w} \quad (11-36)$$

we may combine Eqs. 11-35 and 11-36 to get

$$\begin{aligned} D_{aw} &= \frac{C_a}{C_w + K_c C_w r_{cw}} \\ &= K_H \cdot (1 + K_c r_{cw})^{-1} \end{aligned} \quad (11-37)$$

where K_H is the "true" Henry's Law constant reflecting the equilibrium between the truly dissolved species and its vapor molecules. We should note that the term $(1 + K_c r_{cw})^{-1}$ is simply the fraction of molecules remaining dissolved in this case. Thus the air-water distribution ratio is simply the true K_H multiplied by the fraction of molecules participating in air-water exchange. This result indicates that when colloids are quite abundant in a solution (high r_{cw}) or the chemical-colloid combination of interest exhibits a large K_c , we should expect air-water partitioning to diverge substantially from the simple situation quantified by K_H alone.

Another important ramification of such colloid binding of nonpolar chemicals is that this process diminishes the tendency of such substances to bioaccumulate in aquatic organisms. Leversee et al. (1983) showed this for the uptake of polycyclic aromatic hydrocarbons by *Daphnia*, a freshwater zooplankter. Also, colloid association changes the light-processing characteristics of nonpolar chemicals. For example, Gauthier et al. (1986, 1987) and Backhus and Gschwend (1990) have shown how association of aromatic hydrocarbons with organic colloids diminishes their ability to fluoresce. Clearly, organic chemicals behave differently in many ways when associated with colloids than when they are dissolved in water.

A final major consequence of nonpolar chemical sorption by organic colloids involves efforts to distinguish experimentally the abundances in sorbed and dissolved forms. In batch sorption tests, when we try to separate water from all particles in a soil or sediment suspension, it is practically impossible not to include some colloids with the water. Such colloids go through typical filters and are difficult to sediment, even with intensive centrifugation. As a result, experimental attempts to assess solid-water distribution coefficients virtually always measure colloid-bound molecules with the dissolved ones in the aqueous separate. For that matter, to some extent some water (and associated solute molecules) always remains with the solid separates. As a result, the subsequent processing of measured chemical concentrations for the purpose of K_d calculations should recognize the possibility of such cross-over phases:

$$K_d^{\text{apparent}} = \frac{C_s + C_w V}{C_w + C_c r_{cw}} \quad (11-38)$$

where

C_s is the sorbate concentration on the separated particles ($\text{mol} \cdot \text{kg}^{-1}$),

C_w is the solute concentration in the water ($\text{mol} \cdot \text{L}^{-1}$),

V is the volume of water left with the separated particles ($\text{L} \cdot \text{kg}^{-1}$),

C_c is the sorbate concentration on the colloids ($\text{mol} \cdot \text{kg}^{-1}$), and

r_{cw} is the colloid mass remaining with the bulk of the water ($\text{kg} \cdot \text{L}^{-1}$).

If the solid-water distribution coefficient, defined in Eq. 11-1 as $K_d = C_s \cdot C_w^{-1}$, applies for the separated particles, and we again use a second coefficient, $K_c = C_c \cdot C_w^{-1}$, which applies for the colloidal particles that are not separated from the water, then we may rewrite Eq. 11-38 as

$$K_d^{\text{apparent}} = \frac{K_d + V}{1 + K_c r_{cw}} \quad (11-39)$$

This expression indicates that the apparent solid-water distribution coefficient will only equal the "true" one (as defined by Eq. 11-1) if $V \ll K_d$ and if $K_c r_{cw} \ll 1$. For compounds that do not sorb extensively (low K_d), this result suggests that experimental data may be erroneously high (Fig. 11.12). For chemicals that do tend to sorb (high K_d) and in situations where colloidal phases are substantial (high r_{cw}), batch observations of solid-water partitioning will indicate results lower than K_d (Fig. 11.12). These phase separation difficulties are probably one of the major explanations for the so-called "solids concentration effect" in which K_d appears to decrease with greater and greater loads of total solids (and colloids) in batch sorption systems. Most likely, there is no change in the relative abundances of sorbing nonpolar molecules as the proportions of water and particles are varied (Gschwend and Wu, 1985).

An interesting spinoff of this recognition of colloids in laboratory experiment aqueous phases is the realization that such microparticles and macromolecules undoubtedly exist in natural waters too. As a consequence, one must be concerned

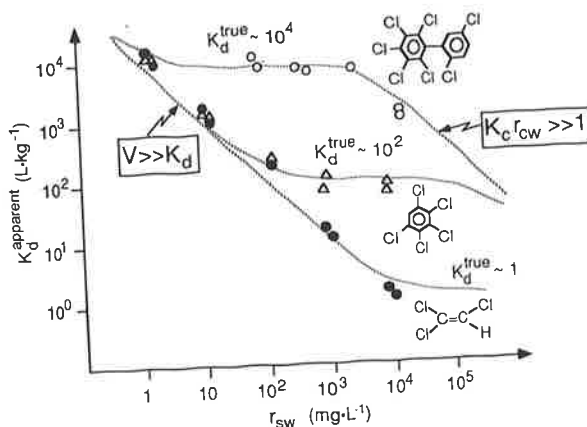


Figure 11.12 Effects of incomplete phase separations on apparent K_d 's of three nonpolar sorbates studied as a function of solids-to-water ratio, r_{sw} , using sediment from the Missouri River with $f_{oc} = 0.72\%$ (data from Gschwend and Wu, 1985, and Gschwend, Brownawell, and Wu, unpublished). Model lines through data are for Eq. 11-39, assuming $V = 0.2 \text{ mL} \cdot \text{g}^{-1}$ and $r_{cw} = 0.02 r_{sw}$. Only the horizontal portions of the curves reflect "true" K_d 's.

that some portion of the molecules of interest moving with fluid flows are attached to colloids (e.g., Enfield et al., 1989). There is evidence that hydrophobic chemicals, like PCBs exist in the surface waters of the Great Lakes, not just as dissolved molecules, but also in association with colloidal phases (Baker et al., 1986). Thus to predict the fate of such chemicals, we may need to consider transport both as dissolved and sorbed-to-colloids forms, and we may need to evaluate transformations remembering that colloid-bound molecules are not free to participate like truly dissolved ones.

11.5 SORPTION OF NEUTRAL ORGANIC CHEMICALS TO POLAR MINERAL SURFACES

In some environments, solids in aquatic systems do not include important amounts of natural organic matter. Consequently, association of organic solutes, especially hydrophobic ones, with mineral surfaces may become significant. This situation exists in groundwater environments where the organic fraction of the aquifer solids is very small (Schwarzenbach and Westall, 1981; Banerjee et al., 1985; Piwoni and Banerjee, 1989). Additionally, clay walls and liners are often used to isolate organic wastes buried below ground; and we may be interested in not only the impact of this low-permeability material on the subsurface hydraulics, but also its suitability for binding organic pollutants and preventing their passage offsite (Boyd et al., 1988). Also, sorption to mineral surfaces may be important when dealing with surface-catalyzed transformations (Ulrich and Stone, 1989). Finally, laboratory glass surfaces and sampling vessels may sorb hydrophobic compounds from aqueous solutions, con-

fusing subsequent data interpretation. Thus, some consideration of the magnitude of the distribution ratio of such compounds between the mineral surface and water and the factors affecting this ratio are in order.

Several investigators have reported "binding" of neutral organic compounds to mineral surfaces (Table 11.3). Although somewhat limited and typically normalized to the mass rather than the surface area of sorbent, these data suggest the following generalizations. First, coarser particles (e.g., silica sand) exhibit less binding than corresponding finer particles made of the same material (e.g., porous silica adsorption of lindane). This is presumably due to the influence of the solid surface area which obviously differs between fine and coarse particles of the same material. Thus, values of sorption coefficients for minerals ($K_{\min} = C_{\min}/C_w$) may be more useful if they are normalized to the solid's surface area rather than its mass (i.e., K_{\min} in units like moles per square meter per moles per liter). The second tendency we see is that for any one sorbent, binding increases within a series of sorbates as a function of their aqueous activity coefficients. Therefore, to predict mineral binding as a function of sorbate properties, it appears that, as for absorption into natural organic matter, we should use characteristics related to γ_w .

Another clue as to the nature of nonionic compound binding to mineral surfaces comes from studies on the effect of temperature on this process. Increasing the system temperature resulted in diminished sorption in three studies (Mills and Biggar, 1969b; Boucher and Lee, 1972; and van Bladel and Moreale, 1974), indicating that the overall process in these cases was exothermic. Since the dissolution of such nonpolar compounds in water is generally an endothermic process (recall Table 5.4), we may reasonably anticipate that some of this energy yield on mineral sorption came from the removal of those chemicals from aqueous solution. Indeed, in all three studies noted above, after accounting for solution enthalpies, the remaining steps in mineral binding of nonpolar sorbates proved to be energetically neutral or even slightly endothermic. From these results it appears that strong molecule:surface interactions are not involved. Unless some moiety is added which can specifically interact with atoms on a solid's surface, the differential extent of mineral adsorption from one chemical to another may be due chiefly to the variations in their aqueous activity coefficients.

A brief description of the chemical nature of mineral surfaces may help us interpret these neutral-chemical sorption phenomena. Most major minerals expose a surface to the exterior which consists of hydroxyls protruding into the medium from a checkboard plane of electron-deficient atoms (e.g., Si, Al, Fe) and electron-rich ligands (e.g., oxygen, carbonate) (Fig. 11.13a). Like water molecules, these surface hydroxyls and ligands prefer to form hydrogen bonds with the molecules adjacent to the mineral surface. We can use data on pure liquid:silica solid attractions reported by Fowkes (1964) to understand the strength of such molecule:surface interactions (Fig. 11.13b). While all sorbates are attracted to the surface by van der Waals or dispersive forces, as functional groups capable of dipole:dipole interaction and H-bonding are added, incrementally stronger attractions per unit surface area of silica are observed. Interestingly, from the point of view of the particular series of sorbates shown in Figure 11.13b, the attraction energy per molecule remains nearly constant. The relatively

TABLE 11.3 Observed Values of K_{\min} for Nonionic Organic Compounds and Inorganic Solids

Adsorbent ^a	Sorbate	$\log \gamma_w^{\text{sat}}$	K_{\min} [mol·kg ⁻¹ ·(mol·L ⁻¹) ⁻¹]	Reference ^b
Porous silica 20°C, 500 m ² /g	Chlorobenzene	4.09	4	1
	1,4-Dichlorobenzene	4.85	6	
	1,2,4-Trichlorobenzene	5.39	8	
	1,2,4,5-Tetrachlorobenzene	6.09	12	
20°C, 890 m ² /g	γ -1,2,3,4,5,6-Hexachloro- cyclohexane (lindane)	5.45	7	2
	β -1,2,3,4,5,6-Hexachloro- cyclohexane	4.99	2	
	Tetrachloroethylene	4.78	13	
	Nitrotoluene	4.04	5	
20°C, 400 m ² /g 23-27°C, 200 m ² /g 23-27°C, 250 m ² /g 23-27°C, 1.6 m ² /g	1,4-Dichlorobenzene	4.85	3.4	3
	Pentachlorobenzene	6.69	26	
Silica sand 5°C	γ -1,2,3,4,5,6-Hexachloro- cyclohexane (lindane)	5.45	0.1	5
	Dieldrin	6.72	2	
	Aldrin	7.20	1.5	
Silica beads 22°C, 0.6 m ² /g	Pyrene	7.09	0.7	7
γ -Alumina 20°C, 120 m ² /g	Chlorobenzene	4.09	0.6	1
	1,4-Dichlorobenzene	4.85	0.9	
	1,2,4-Trichlorobenzene	5.39	1.5	
	1,2,4,5-Tetrachlorobenzene	6.09	2.2	

1,4-Dichlorobenzene 4.83
 1,2,4-Trichlorobenzene 5.39
 1,2,4,5-Tetrachlorobenzene 6.09

Kaolinite 20°C, 12 m ² /g	Chlorobenzene	4.09	0.6	1
	1,4-Dichlorobenzene	4.85	1.1	
	1,2,4-Trichlorobenzene	5.39	2.4	
	1,2,4,5-Tetrachlorobenzene	6.09	4.9	
Unknown 22°C, 12 m ² /g	Aldrin	7.20	3	6
	1,2,4-Trichlorobenzene	5.39	0.3	7
	Pyrene	7.09	50	
	Perylene	8.1	1.3 × 10 ⁵	
	Methyl perylene	8.7	2.0 × 10 ⁵	
Montmorillonite	Aldrin	7.20	3	6
Ca-Montmorillonite 20°C	γ-1,2,3,4,5,6-Hexachloro- cyclohexane (lindane)	5.45	3	2
	β-1,2,3,4,5,6-Hexachloro- cyclohexane	4.99	4	
26.5°C, 760 m ² /g	Fenuron	2.32	8	8
	Monuron	3.13	13	
	Diuron	4.16	23	9
Na-montmorillonite 25°C, 610 m ² /g	Fenuron	2.32	14	
	Monuron	3.13	24	
	Fenuron	2.32	8	8
	Monuron	3.13	13	
	Phenol	1.7	0.2	10
26.5°C, 760 m ² /g	Ethanol	~0	0.2	
	1,4-Dioxane	~0	0.5	
	Urea	~0	0.6	
800 m ² /g				

^aTemperature and surface area, if known.

^b1. Schwarzenbach and Westall, 1981. 2. Mills and Biggar, 1969a. 3. Estes et al., 1988. 4. Szecsody and Bales, 1989. 5. Boucher and Lee, 1972. 6. Yaron et al., 1967. 7. Backhus, 1990. 8. van Bladel and Moreale, 1974. 9. Bailey et al., 1968. 10. Zhang et al., 1990.

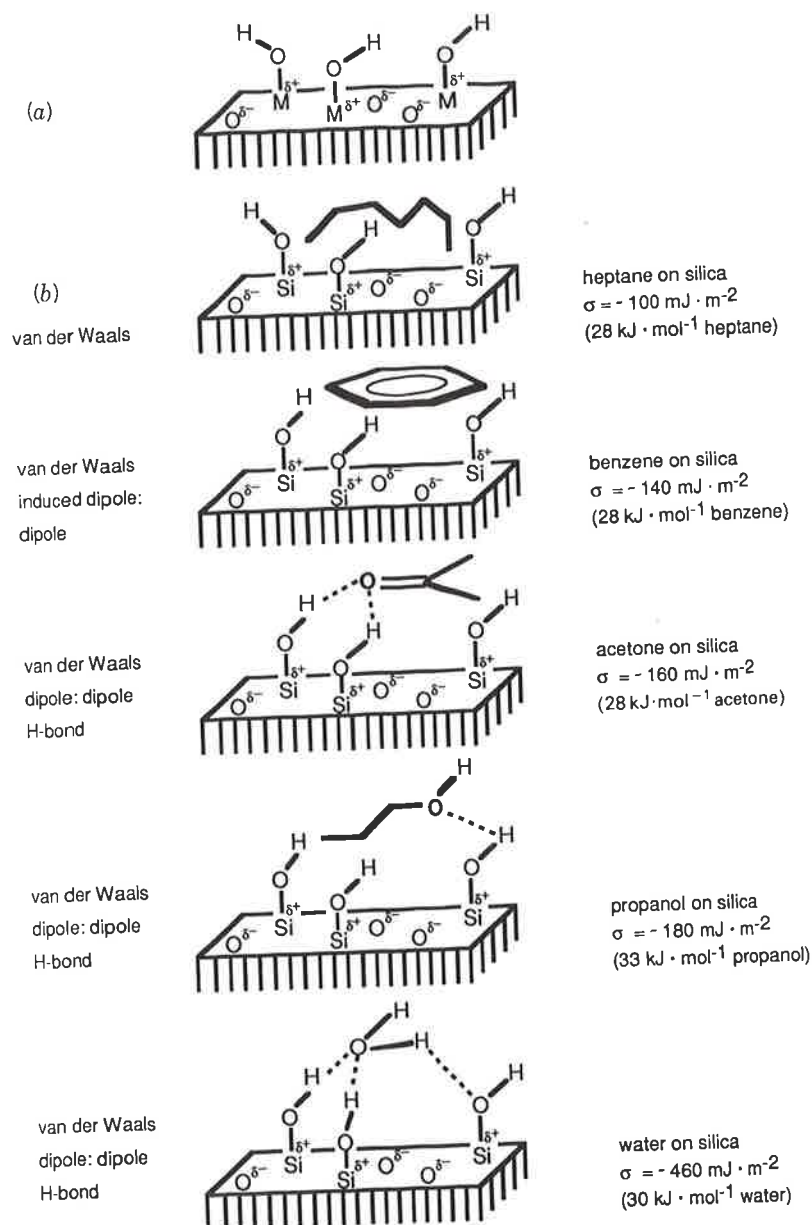


Figure 11.13 (a) A schematic view of a mineral surface exhibiting loci of partial positive charges where metal atoms occur (M), partial negative charges where linking anions occur (shown as oxygen atoms), and hydroxyl substituents extending to the exterior. (b) Interactions of organic chemicals wetting silica surfaces and a measure of the interaction strengths derived from surface tension data (Fowkes, 1964).

small water molecules make up what they lack in dispersive attraction by using H-bonding. Thus, one anticipates that water is extremely favored in competitions with nonionic organic sorbates for positions on such minerals surfaces, and the energy change on adsorbing such organic chemicals directly to the solid must also reflect the desorption of water from the same area.

The strong interactions of water molecules with solid surfaces causes the water molecules near the surface to be oriented. This organizing effect seems to extend for several layers of water out toward the bulk medium (Drost-Hansen, 1969; Etzler and White, 1987). Thus, a complete image of organic chemical "binding" to minerals from aqueous solutions, especially for nonpolar compounds (i.e., the ones least able to displace adsorbed water), may need to include the advantage gained upon transfer of these compounds into the ordered water layer immediately adjacent to solid surfaces. The volume of this so-called "vicinal water" per mass of sorbent would be directly related to the intraparticle porosity and surface area and consequently should be greater for porous silica (~ 0.5 mL/g) than for quartzite sand (< 0.01 mL/g) and greater for expandable montmorillonite (~ 1 mL/g) than for the two-layer clay kaolinite (< 0.02 mL/g). Such volumes may approach a milliliter per gram in highly porous solids (Ogram et al., 1985; Mikhail et al., 1968a, b) and may reflect the water's behavior for nanometers away from the solid surface. In view of this concept of vicinal water, nonpolar "binding" to minerals may involve not only the exchange of organic sorbates with water molecules at the surface, but also the partitioning between relatively disorganized bulk water and this special volume of ordered water near the solid's surface.

In light of these observations, we may be able to find linear free-energy relationships which are suitable for estimating new K_{\min} values. If the tendency of sorbates to escape aqueous solutions is an important factor, as it appears from the very limited available data, we expect the free energy of sorption of neutral organic compounds on minerals to be inversely related to the free energy of aqueous dissolution of those same (liquid) chemicals. This expectation is supported by the available data (Fig. 11.14) when we examine $\log K_{\min}$ (proportional to the sorption free energy) versus $\log \gamma_w$ (reflecting the free energy of dissolution). For both silica and kaolinite sorbents, a correlation is seen of the form

$$\log K_{\min}(\text{L} \cdot \text{m}^{-2}) \simeq a \cdot \log \gamma_w + b \quad (11-40)$$

where a and b are fitted coefficients. One recent study found that $a \simeq 1.4$ and $b \simeq -11$ for a small set of organic sorbates interacting with silica and kaolinite (Backhus, 1990). Of course, one should not necessarily infer that this expression applies for other mineral types (e.g., carbonates, iron oxides). Although the data are very few and exhibit substantial scatter, this result does suggest it may be feasible to predict mineral surface binding coefficient from properties like γ_w^{sat} , $C_w^{\text{sat}}(\text{l}, \text{L})$ or K_{ow} of the sorbates.

Based on this limited understanding of the magnitudes of K_{\min} values, one may be tempted to try to predict the conditions under which nonpolar chemical sorption to mineral surfaces dominates association with natural organic matter (i.e.,

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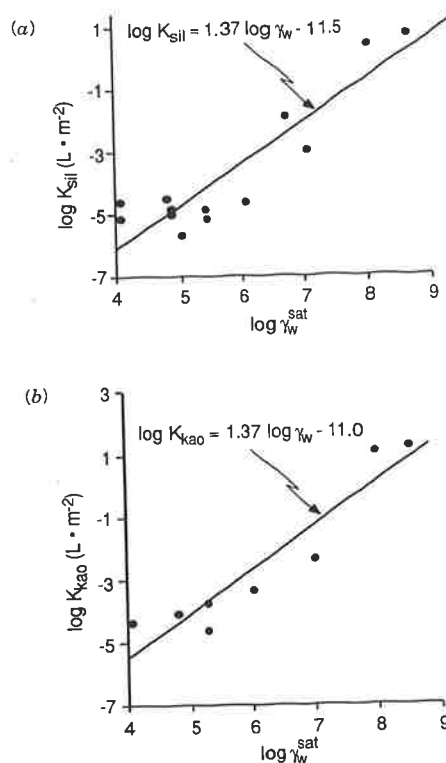


Figure 11.14 Relationship of $\log K_{\text{min}}$ and $\log \gamma_w$ as illustrated by the data of Yaron et al. (1967), Mills and Biggar (1969a), Schwarzenbach and Westall (1981), Estes et al. (1988), Szecsody and Bales (1989), and Backhus (1990): (a) for silica sorbents and (b) for kaolinite sorbents.

$A \cdot K_{\text{min}} > f_{\text{om}} \cdot K_{\text{om}}$). However, since sorption of nonpolar sorbates to mineral surfaces is an adsorption phenomenon, it is probably subject to competitive effects arising from the presence of other sorbates. Included in this competition for space on mineral surfaces is the natural organic matter itself. These natural materials are known to attach to kaolinite, iron oxides, and other minerals, especially when the inorganic surfaces are positively charged (Tipping, 1981; Davis, 1982). As a consequence, the available mineral surface area may be inversely related to f_{om} . Thus, we must know not only when $A \cdot K_{\text{min}} > f_{\text{om}} \cdot K_{\text{om}}$, but also how A varies with f_{om} in the system.

Some empirical approaches have been suggested to indicate when mineral surface sorption of nonpolar compounds starts to become important. First, sorption data appear to fit the pattern exhibited by pyrene in Fig. 11.5 as long as $f_{\text{om}} > 0.002$ to 0.004 (Schwarzenbach and Westall, 1981; Banerjee et al., 1985). Below this cutoff, the influences of mineral surfaces start to be felt. On the other hand, experiments to test

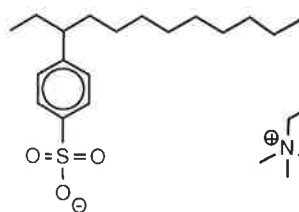
for the extent of sorption before and after soil organic carbon oxidation indicate that this natural organic matter continues to play an important role even to virtually unmeasurable levels (Karickhoff, 1984; Lion et al., 1990). Unfortunately, these "thresholds" appear to vary as a function of the sorbate's hydrophobicity (Karickhoff, 1984; Banerjee et al., 1985). Competition between sorption to natural organic matter and to mineral surfaces is probably also a function of other soil or sediment properties, such as the proportion of swelling clays present with their very large specific surface areas (Karickhoff, 1984). Thus, the ratio of A to f_{om} is undoubtedly important. In sum, at f_{om} less than about 0.002 we should begin to consider sorption to mineral surfaces as contributing to the total picture, but this additional sorption mechanism may or may not become dominating depending on the properties of the sorbate and solid mixture of interest.

11.6 ADSORPTION OF IONIZABLE ORGANIC CHEMICALS FROM AQUEOUS SOLUTIONS

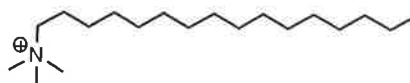
Influences of Charged Moieties Present in Organic Compounds on K_d

Now we begin to consider organic species that exhibit at least one ionic group in their structure (e.g., $-\text{COO}^-$, $-\text{NH}_3^+$, $-\text{SO}_3^-$). Much of the work on this topic has been performed by investigators interested in surfactants, since the inclusion of a charged moiety on an otherwise nonpolar chemical skeleton renders the resultant compound *amphiphilic* (part liking water, part disliking water) and capable of participating in many interesting interfacial phenomena. Also, a good deal of progress has been made by researchers studying the chemistry of inorganic surfaces (e.g., metal oxides) and how these minerals are affected by organic *ligands* (compounds that bind metals; from the Latin *ligare*: to bind).

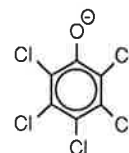
When organic chemicals include structural components that are ionized, for example,



3-Dodecylbenzene sulfonate
(anionic detergent)



Hexadecyl trimethyl ammonium
(cationic detergent, disinfectant)



Pentachlorophenolate
(wood preservative)

a variety of new effects become important insofar as the interactions of these sorbates with solid surfaces are concerned. This is largely due to two phenomena that we have not considered for neutral sorbates: (1) the electrostatic interactions of charged

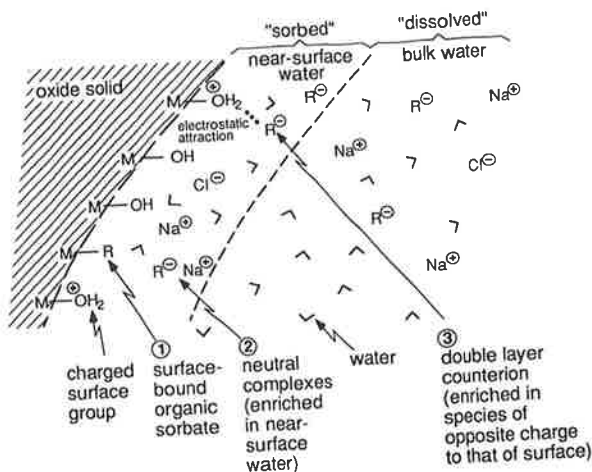


Figure 11.15 A positively charged oxide particle in water attracts anionic species including organic ones (e.g., R^-) to the near-surface water. Some of these anionic species may also react with the surface, displacing other ligands (e.g., H_2O or OH^-), to form surface-bound sorbate. M in the solid refers to atoms like Si, Al, or Fe.

molecules with charged sites on the sorbent (i.e., giving rise to the product $C_{ic} \cdot \sigma_{ic} \cdot A$ in the numerator of Eq. 11-9), and (2) exchange reactions with ligands previously bound to the solid (i.e., contributing to the terms $C_{rxn} \cdot \sigma_{rxn} \cdot A$ in Eq. 11-9).

First, owing to the ubiquitous phenomenon of ionizable surface groups on wet particles, virtually every solid presents a charged surface to the aqueous solution. If this surface charge is of opposite sign (e.g., positive) to that exhibited by an organic functional group (e.g., negative), then there will be an electrostatic attraction (ΔG_{elect}) between the organic sorbate in the bulk solution and the particle surface (Fig. 11.15). Such organic ions will accumulate in the thin film of water surrounding the particle as part of the population of charges in solution balancing the charges on the solid surface. Conversely, organic molecules with charges of like sign as the surface will be repulsed from the near-surface water. These electrostatic effects act similarly for all charged sorbates.

The second interaction involves chemical bonding of the organic compound to the surface or to some component of the solid phase. As depicted in Fig. 11.15, this may involve displacing some ligand previously bound to the surface (e.g., OH^- in Fig. 11.15). Alternatively, such a reaction could look more like the condensation reaction shown in Figure 11.2. Such a surface reaction involves another free energy change (ΔG_{rxn}). We must note that a surface reaction forms a second sorbed species which is distinct from like-structured organic ions dissolved in the near-surface water (e.g., $M-R \neq M-OH_2^+ \dots R^-$).

Finally, we will find that some charged organic compounds include a sufficiently large hydrophobic portion in their structure that transfer into near-surface (i.e., vicinal) water is favored (i.e., due to a negative $\Delta G_{hydrophob}$) even in the absence of surface

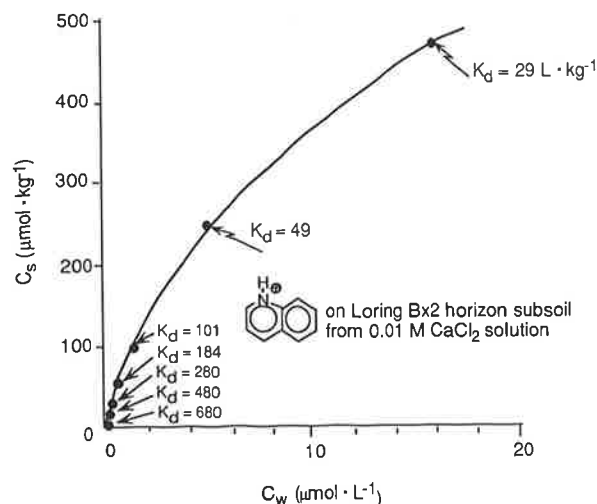


Figure 11.16 Nonlinear sorption isotherm exhibited by quinoline on a subsoil of $f_{om} \approx 0.48\%$, surface area $\approx 30.5 \text{ m}^2/\text{g}$, and cation exchange capacity of $8.4 \text{ mmol}/100\text{g}$ (data from Zachara et al., 1986).

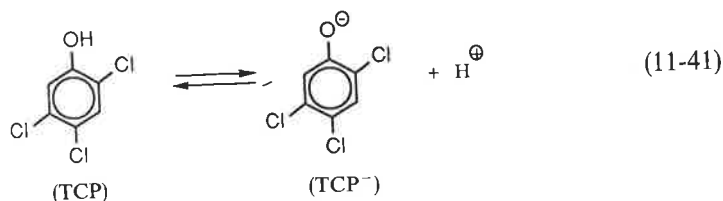
charges or reactive surface sites. Such sorption requires the cotransfer of a counterion (e.g., Na^+ with R^- in Fig. 11.15) to maintain local electroneutrality.

Experiments typically show that the isotherms of charged organic sorbates are decidedly nonlinear (Fig. 11.16). Said another way, the solid–water distribution ratio changes markedly as a function of the sorbate’s own dissolved concentration. The extent of solid association of charged organic compounds also varies as a function of factors like solution pH, since this property governs both the presence of charges on mineral surfaces and the fraction of sorbate in an ionized form. Solution ionic strength and ionic composition also affect the sorption of charged organic chemicals, especially if inorganic ions compete with organic ones for binding sites. Obviously, the mineral composition of the sorbent is a key factor. Not surprisingly, all of these factors make the *a priori* estimation of charged organic chemical sorption to natural soils and sediments much more difficult and complex than for neutral compounds where everything is usually reducible to a few key factors (e.g., γ_w and f_{om}). In the following sections, we examine in more detail the nature of the interactions of charged molecules with charged surfaces and discuss how we might estimate the extent of such (ad)sorption.

Influence on K_d of Organic Compound Speciation in Solution

Before we discuss the sorbate–sorbent interactions that control charged organic species sorption, let us briefly examine the impact of solution pH on the sorption of substances that can be protonated or deprotonated to varying extents depending on

their pK_a (recall Chapter 8). As a result of rapid acid-base interconversion, the solution may contain two (or more) organic species, a neutral one, and its conjugate acid or base. Each of these solution species will be involved in its own sorptive exchange phenomena as we noted before (e.g., Eqs. 11-10 through 11-13). Thus, we must begin analyzing ionizable chemical sorption by realizing what fraction of that chemical occurs in its charged, as opposed to its neutral form. For example, if we consider sorption of phenolic compounds like 2,4,5-trichlorophenol ($pK_a = 6.94$):



we may calculate that the fraction of this compound in the neutral form at any pH is (after Eq. 8-16):

$$\alpha_a = \frac{1}{1 + K_a/[\text{H}^+]} \quad (11-42)$$

Similarly, the proportion present as the charged species is

$$(1 - \alpha_a) = \frac{K_a/[\text{H}^+]}{1 + K_a/[\text{H}^+]} \quad (11-43)$$

Now we proceed by evaluating the solid interactions of each of these dissolved species separately. In this case, we anticipate that the neutral species will sorb to natural solids containing natural organic matter just like any other nonionic organic chemical (recall Eq. 11-16):

$$K_d(\text{TCP}) = \frac{[\text{TCP}]_{\text{om}}}{[\text{TCP}]_w} \cdot f_{\text{om}} \quad (11-44)$$

where $[\text{TCP}]_{\text{om}}$ is the concentration of the nonionized trichlorophenol in the solid organic matter, and $[\text{TCP}]_w$ is the concentration of the nonionized trichlorophenol in the water. We may similarly define for the anionic phenolate species:

$$K_d(\text{TCP}^-) = \frac{[\text{TCP}^-]_{\text{om}}}{[\text{TCP}^-]_w} \cdot f_{\text{om}} \quad (11-45)$$

where, in this case, we assume the major sorption mechanism for the phenolate is dissolution into natural organic matter. Next, we may reasonably expect that the presence of a charge on the deprotonated phenol species will cause this molecule to be much more water-soluble than its conjugate acid. Therefore, such ionized phenol

molecules exhibit correspondingly less tendency to go from solution into particulate organic matter:

$$K_{om}(TCP^-) \ll K_{om}(TCP) \quad (11-46)$$

We would expect $K_{om}(TCP^-)$ to be about three orders of magnitude less than $K_{om}(TCP)$ since the K_{ow} of phenolate is about that much less than the K_{ow} of the corresponding phenol (see Chapter 8 or fragment constants in Lyman et al., 1982). If the phenolate species does not sorb by another major mechanism besides dissolving in the natural organic matter, and this appears to be true for many natural solids which are primarily negatively charged at natural water pH's, then we may estimate the total sorption of the trichlorophenol using a distribution ratio:

$$K_d(TCP \text{ plus } TCP^-) = \frac{([TCP]_{om} + [TCP^-]_{om}) \cdot f_{om}}{[TCP]_w + [TCP^-]_w} \quad (11-47)$$

where we have written K_d as the ratio of all major sorbed species divided by the sum of all the forms in the water (TCP_w and TCP^-_w). Rearranging and substituting with the K_a and K_{om} expressions defined above, we deduce

$$K_d(TCP \text{ plus } TCP^-) = \frac{\left[\frac{[TCP]_{om}}{[TCP]_w} + \frac{[TCP^-]_{om}}{[TCP^-]_w} \right] \cdot f_{om}}{1 + \frac{[TCP^-]_w}{[TCP]_w}} \quad (11-48)$$

$$= \frac{\left[\frac{[TCP]_{om}}{[TCP]_w} + \frac{[TCP^-]_{om} \cdot K_a}{[TCP^-]_w [H^+]} \right] \cdot f_{om}}{1 + \frac{K_a}{[H^+]}} \quad (11-49)$$

$$= \frac{[K_{om}(TCP) + K_{om}(TCP^-) \cdot K_a / [H^+]] \cdot f_{om}}{1 + \frac{K_a}{[H^+]}} \quad (11-50)$$

As long as we are interested in cases where the solution pH is less than about two units above the acid's pK_a (i.e., $K_a/[H^+] \ll 1,000$), then we may neglect the involvement of TCP^- with the particulate organic matter:

$$K_d(TCP \text{ plus } TCP^-) \simeq \frac{K_{om}(TCP) \cdot f_{om}}{1 + \frac{K_a}{[H^+]}} \quad (11-51)$$

This result is equivalent to

$$K_d(\text{TCP plus TCP}^-) = \alpha_a \cdot K_d(\text{TCP}) \quad (11-52)$$

Equation 11-52 implies that sorption of this trichlorophenol isomer will depend not only on the tendency of the ionized phenol to associate with particulate organic matter [$K_d(\text{TCP})$], but also on the fraction (α_a) of nondissociated species in aqueous solution at a given pH. The accuracy of this result is illustrated in Figure 11.17. Using a lake sediment of f_{om} near 19%, Schellenberg and co-workers (1984) measured the solid-water distribution coefficient of 2,4,5-trichlorophenol at several solution pH's. They saw diminished sorption at higher pH, and this trend in K_d closely mirrored the change in TCP present in its protonated form. Further, the K_d found at pH's well below TCP's pK_a matched the result these investigations expected for nonionized TCP sorption to the particulate organic matter.

When the solution pH is such that the anionic species finally becomes much more abundant than its neutral counterpart in solution, we cannot neglect the sorption of TCP^- (Jafvert, 1990; Jafvert et al., 1990). Unfortunately $K_{om}(\text{TCP}^-)$ is not constant at all solution pH's and ionic conditions. In some part this is due to the variation in solid charging as solution pH changes, causing differential electrostatic repulsions at varying pH. Various ions (e.g., Ca^{2+} versus Na^+) also affect the value of $K_{om}(\text{anions})$ owing to the differential formation of ion pairs [e.g., $\text{Ca}^{2+}(\text{phenolate}^-)_2$].

Thus in cases where an organic chemical may be present as more than one species in solution, we must consider the sorptive interactions of each of these species. We

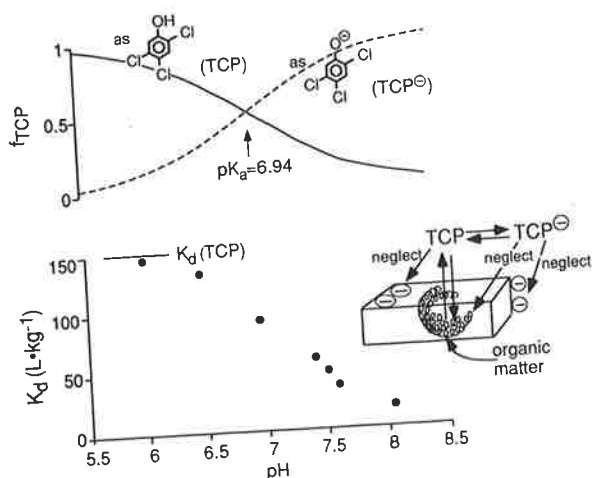
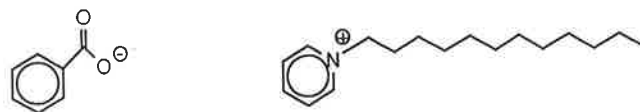


Figure 11.17 2,4,5-Trichlorophenol ionization (upper) and sorption to a lake sediment (lower) as a function of solution pH (data from Schellenberg et al., 1984). Inset indicates the importance of TCP interaction with particulate organic matter, in this case, relative to other sorption processes for TCP or TCP^- .

may often find that the overall solid-water distribution coefficient can be estimated from information on the dominant sorption interaction and the fraction of molecules available to participate in that interaction. In the following sections we focus on the processes governing the sorption of ionized organic species, thereby enabling us to determine when sorbed species besides nonionized molecules in natural organic matter become dominant.

Sorption of Charged Organic Species

Let us continue our discussion by evaluating the sorption of the *charged organic species themselves*. We first examine cases where specific chemical reactions (i.e., bond breaking and making) with the solid are *not* important to K_d . For example, for now we consider "monodentate" compounds like benzoate or unreactive ones such as dodecylpyridinium:



but not bidentate ones like salicylate or compounds like aniline with its reactive amine moiety:



We make this distinction because "monodentate" compounds (i.e., those with a "single tooth" with which to bond to atoms on the surface of solids) seem to sorb more as counterions dissolved in the near-surface thin film of water than as surface-bound species. The "polydentate" compounds like salicylate form, not only the near-surface counterion species, but also nonnegligible quantities of surface-bound sorbates (Yost et al., 1990). Quaternary ammonium compounds like dodecyl pyridinium do not retain any nonbonded electrons with which to bond to components of the solid phase, in contrast to aniline which can react with carbonyl moieties included in particulate organic matter (Hsu and Bartha, 1976). Before we can treat surface-bound forms, it is useful to know how to handle electrostatic influences in isolation.

Surface Charges on Solids in Water To evaluate the importance of charged organic compound interchange between the bulk aqueous solution and the thin layer of water surrounding a charged particle (Fig. 11.18), we need to know how many charges are on the surfaces of solids. The adjacent surficial layer of water (i.e., Region II in Fig. 11.18) contains an excess of ions, called counterions (e.g., Na^+ in Fig. 11.18), that carry charge equal in magnitude and opposite in sign to that exhibited by the particle surface (i.e., Region I in Fig. 11.18). The thickness of this ion-rich water layer, which is sometimes called the *diffuse double layer*, varies inversely with the ionic strength

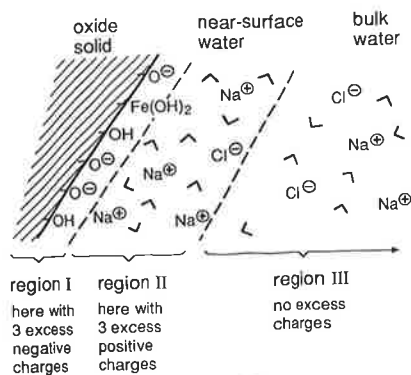
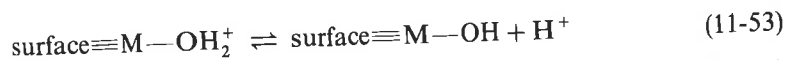


Figure 11.18 A schematic view of the accumulation of counterions in a narrow solution volume adjacent to charged particle surfaces. Region I depicts the charged surface layer formed by reactions of surface groups with acids or bases (e.g., $M-OH + OH^- \rightleftharpoons M-O^- + H_2O$) and with certain strongly sorbed ions [e.g., $M-O^- + Fe(OH)_2^+ \rightleftharpoons M-O-Fe(OH)_2$]. Region II is the diffuse double layer in which counterions (e.g., Na^+) accumulate in excess over bulk solution concentrations to match the net charge on the solid surface. Region III is the aqueous solution outside the diffuse double layer where electroneutrality is achieved by the sum of cation charges equaling the sum of anion charges.

of the solution. The e^{-1} characteristic width is given by $0.28 \times I^{-0.5}$ nm, where I is the solution's ionic strength in molar units (Morel, 1983). For typical ionic compositions of natural waters (10^{-3} – 0.5 M), this means that most [i.e., $(1 - e^{-1}) \cdot 100\% = 63\%$] of the counterions are packed into a layer of water between 0.3 and 10 nm thick, and nearly all [i.e., $(1 - e^{-3}) \cdot 100\% = 95\%$] are within 1–30 nm of the surface. It is worth noting that this range is very similar to the 1–10 nm range believed to reflect ordered vicinal water (Drost-Hansen, 1969); thus, this is indeed a very special microscopic water environment.

For charged species that do not react with the surface, we recognize that the extent of their accumulation in this layer of water is caused at least in part by electrostatic attractions or repulsions (ΔG_{elect}). A major factor in governing these attractions is the abundance of charges on the particle's surface. Several kinds of surfaces can be envisioned; here we especially consider: (1) oxides or oxyhydroxides, (2) aluminosilicates or clay minerals, and (3) natural organic matter.

For natural solids that are *oxides or oxyhydroxides* (e.g., quartz, SiO_2 ; goethite, $FeOOH$; alumina, Al_2O_3), their water-wet surface is covered by hydroxyl groups (recall Fig. 11.13). These hydroxyl moieties can undergo proton-exchange reactions with the aqueous solution much like dissolved acids:



where M refers to an atom like Si, Fe, or Al at the particle surface, and \equiv refers to

the attachments of that atom to the solid. We may define acid-base equilibrium constants for those reactions:

$$K_{a1} = \frac{[=\text{MOH}][\text{H}^+]}{[=\text{MOH}_2^+]} \quad (11-55)$$

$$K_{a2} = \frac{[=\text{MO}^-][\text{H}^+]}{[=\text{MOH}]} \quad (11-56)$$

These surface acid equilibrium constants differ from their solution counterparts in that they reflect both an *intrinsic* reactivity of the particular O—H bond and an electrostatic free energy of moving H^+ to and from a charged surface:

$$K_{a1} = K_{a1}^{\text{int.}} e^{F\psi/RT} \quad (11-57)$$

$$K_{a2} = K_{a2}^{\text{int.}} e^{F\psi/RT} \quad (11-58)$$

where

F is the Faraday constant ($96,485 \text{ C} \cdot \text{mol}^{-1}$),

ψ is the surface potential relative to the bulk solution (V or $\text{J} \cdot \text{C}^{-1}$),

R is the molar gas constant ($8.31 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$), and

T is the absolute temperature (K).

At higher and higher pH's, ψ becomes less and less positive as reaction 11-53 proceeds to the right and more and more negative as reaction 11-54 continues to the right. This variation in surface charge buildup makes it increasingly more difficult to move H^+ away from an oxide surface as solution pH is increased. The magnitude of this effect is calculated with the exponential terms in Eqs. 11-57 and 11-58.

It is also possible for some other inorganic species (e.g., Fe^{+3} or PO_4^{-3}) to bond with the surface [e.g., $\text{Fe}(\text{OH})_2^+$ bound in Region I of Fig. 11.18]; in such a case, these inorganic ions along with H^+ and OH^- are responsible for establishing the extent of charging on the solid surface. The combination of ions responsible for this charge formation are called "potential (ψ) determining." For now, we neglect specific inorganic adsorption other than H^+ and OH^- and their effects on surface charge (e.g., see Dzombak and Morel, 1990, for examples of specific sorption and its associated impact on surface charge for hydrous ferric oxide).

For the case at hand, it is easy to see that the abundance of $=\text{MOH}_2^+$ and $=\text{MO}^-$ species on the solid surface control the surface's charge. The concentration of this charge, σ_{ie} (mol charges $\cdot \text{m}^{-2}$) can be estimated (neglecting other specifically sorbed species):

$$\sigma_{ie} = [=\text{MOH}_2^+] - [=\text{MO}^-] \quad (11-59)$$

where the surface species concentrations are given in units of mole per meter squared

of exposed surface. When these two surface species are present in equal concentration, the surface exhibits zero net charge (also $\psi = 0$); we call the solution pH that establishes this condition, the pH of zero point of charge, or pH_{zpc} . This pH_{zpc} can be calculated if we know the intrinsic acidities of =MOH_2^+ and =MOH :

$$[\text{=MOH}_2^+] = [\text{=MO}^-] \quad \text{at } \text{pH}_{\text{zpc}} \quad (11-60)$$

Substituting from Eqs. 11-55 to 11-58 and recalling $\psi_{\text{zpc}} = 0$, we have

$$[\text{=OH}][\text{H}^+]_{\text{zpc}}(K_{\text{a1}}^{\text{int}})^{-1} = [\text{=OH}][\text{H}^+]_{\text{zpc}}^{-1}(K_{\text{a2}}) \quad (11-61)$$

Simplifying Eq. 11-61 allows us to relate pH_{zpc} and the intrinsic acidities of the surface:

$$[\text{H}^+]_{\text{zpc}}^2 = K_{\text{a1}}^{\text{int}} K_{\text{a2}}^{\text{int}} \quad (11-62)$$

$$[\text{H}^+]_{\text{zpc}} = (K_{\text{a1}}^{\text{int}} K_{\text{a2}}^{\text{int}})^{0.5} \quad (11-63)$$

$$\log [\text{H}^+]_{\text{zpc}} = 0.5(\log K_{\text{a1}}^{\text{int}} + \log K_{\text{a2}}^{\text{int}}) \quad (11-64)$$

$$\text{pH}_{\text{zpc}} = 0.5(\text{p}K_{\text{a1}}^{\text{int}} + \text{p}K_{\text{a2}}^{\text{int}}) \quad (11-65)$$

Equation 11-65 shows that an oxyhydroxide's pH_{zpc} is midway between the intrinsic $\text{p}K_{\text{a}}$'s of its surface groups. Now, when the aqueous solution pH is below the pH_{zpc} , we have the condition $[\text{=OH}_2^+] > [\text{=O}^-]$, and the solid exhibits a net positive surface charge. Conversely, when we are above the solid's pH_{zpc} , then $[\text{=O}^-] > [\text{=OH}_2^+]$, the surface is negatively charged, and it becomes increasingly so at higher pH.

Our task now is to estimate the concentration of surface charge for cases that interest us as a function of solid and solution properties. Table 11.4 shows how this can be done by solving for the abundances of the important surface species, =OH_2^+ and =O^- , using two sets of information: (1) knowledge of the intrinsic acidities for the oxide of interest, and (2) the feedback relationship of surface potential on surface charge density. Figure 11.19 illustrates the results of such calculations on charge density at pH's below and above an oxide's pH_{zpc} for aqueous solutions of $I = 0.001$ and 0.5 M . These results may be understood with a specific example. If we were interested in iron oxide with a $\text{p}K_{\text{a1}}^{\text{int}}$ of 7 (Table 11.5) and a surface hydroxyl density of $2 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$, we could estimate that this solid would have about $2 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2}$ of positive charges on its surface at pH 6 in freshwater of $I = 10^{-3} \text{ M}$ (i.e., $\sim 10\%$ as M=OH_2^+ in Fig. 11.19). In salty water of $I = 0.5 \text{ M}$ and pH = 6, the same solid would have a little more than $1 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ of positive charges (i.e., $\sim 50\%$ as M=OH_2^+ in Fig. 11.19). If the solution pH was 7 instead of 6, the surface charge density would decrease by about a factor of 2. It would not be until pH was increased to above 8 [$\text{pH}_{\text{zpc}} = 0.5(7 + 9) = 8$] that this solid would start to show a net negative surface charge. Table 11.5 shows some other important oxide minerals common in aquatic environments, their typical surface areas, and their

TABLE 11.4 Estimating the Surface Charge σ_{ie} of Oxides When H^+ and OH^- Are the Potential-Determining Ions

$$\sigma_{ie}(\text{mol charges} \cdot \text{m}^{-2}) = [\equiv\text{MOH}_2^+] - [\equiv\text{MO}^-] \quad (11-59)$$

where

$[\equiv\text{MOH}_2^+]$ is the concentration of protonated surface sites ($\text{mol} \cdot \text{m}^{-2}$), and
 $[\equiv\text{MO}^-]$ is the concentration of deprotonated surface sites ($\text{mol} \cdot \text{m}^{-2}$).

When $[\equiv\text{MOH}_2^+] > [\equiv\text{MO}^-]$, σ_{ie} is positive, indicating a net positive surface charge; conversely, when the $[\equiv\text{MO}^-] > [\equiv\text{MOH}_2^+]$, σ_{ie} is negative and its absolute value reflects the concentration of negative sites.

Using acidity relationships (Eqs. 11-55 through 11-58)

$$\sigma_{ie} = [\equiv\text{MOH}][H^+]K_{a1}^{-1} - [\equiv\text{MOH}][H^+]^{-1}K_{a2} \quad (11-66)$$

$$\sigma_{ie} = [\equiv\text{MOH}][H^+](K_{a1}^{\text{int}})^{-1}e^{-F\psi/RT} - [\equiv\text{MOH}][H^+]^{-1}K_{a2}^{\text{int}}e^{F\psi/RT} \quad (11-67)$$

where

K_{a1}^{int} and K_{a2}^{int} are the intrinsic equilibrium constants quantifying the extent of proton exchange in the absence of charging the surface,

ψ is the surface potential ($V = J \cdot C^{-1}$),

R is the molar gas constant ($8.31 J \cdot \text{deg K}^{-1} \text{mol}^{-1}$),

T is the absolute temperature (K), and

F is the Faraday constant ($96,485 C \cdot \text{mol}^{-1}$).

The surface charge and surface potential are related (Stumm and Morgan, 1981):

$$\psi = \frac{2RT}{zF} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] \quad (11-68)$$

where

z is the valence of ions in the background electrolyte (e.g., NaCl, $z = 1$),

ϵ is the dielectric constant of water ($7.2 \times 10^{-10} C \cdot V^{-1} m^{-1}$ at 25°C), and

I is the solution ionic strength ($\text{mol} \cdot \text{L}^{-1}$; 10^{-3} is needed to convert L to m^3).

Substituting Eq. 11-68 into 11-67 yields:

$$\begin{aligned} \sigma_{ie} = & [\equiv\text{MOH}][H^+](K_{a1}^{\text{int}})^{-1} \exp \left(-\frac{2}{z} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] \right) \\ & - [\equiv\text{MOH}][H^+]^{-1}(K_{a2}^{\text{int}}) \exp \left(+\frac{2}{z} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] \right) \end{aligned} \quad (11-69)$$

(Continued)

TABLE 11.4 (Continued)

Well below the pH_{zpc} ($[≡MOH_2^+] \gg [≡MO^-]$), Eq. 11-69 simplifies to:

$$\sigma_{ie} = [≡MOH][H^+](K_{a1}^{int})^{-1} \exp\left(-\frac{2}{z} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] \right) \quad (11-70a)$$

or

$$\log \sigma_{ie} + \frac{2}{2.303z} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] - \log [≡MOH_0 - |\sigma_{ie}|] = -pH + pK_{a1}^{int} \quad (11-70b)$$

At $T = 25^\circ\text{C}$, $I = 10^{-3} \text{ M}$, a 1:1 background electrolyte ($z = 1$), and with an initial hydroxyl site density ($[≡MOH_0]$) of $2 \times 10^{-6} \text{ mole/m}^2$, this becomes:

$$\log \sigma_{ie} + 0.868 \sinh^{-1}(9.05 \times 10^7 \sigma_{ie}) - \log(2 \times 10^{-6} - |\sigma_{ie}|) = -pH + pK_{a1}^{int} \quad (11-71)$$

which can be solved for σ_{ie} at pH's below the solid's pK_{a1}^{int} .

At $T = 25^\circ\text{C}$, $I = 0.5 \text{ M}$, a 1:1 background electrolyte, and with an initial hydroxyl site density of $2 \times 10^{-6} \text{ mole/m}^2$, this becomes:

$$\log \sigma_{ie} + 0.868 \sinh^{-1}(4.05 \times 10^6 \sigma_{ie}) - \log(2 \times 10^{-6} - |\sigma_{ie}|) = -pH + pK_{a1}^{int} \quad (11-72)$$

Conversely, well above pH_{zpc} ($[≡MO^-] \gg [≡MOH_2^+]$), we have from 11-67:

$$\log \sigma_{ie} + \left(\frac{2}{2.303z} \sinh^{-1} \left[\left[\frac{\pi F^2 10^{-3}}{2\epsilon RTI} \right]^{0.5} \sigma_{ie} \right] \right) + \log [≡MOH_0 - |\sigma_{ie}|] = -pH + pK_{a2}^{int} \quad (11-73)$$

At $T = 25^\circ\text{C}$, $I = 0.5 \text{ M}$, a 1:1 background electrolyte, and with an initial hydroxyl site density of $2 \times 10^{-6} \text{ mole/m}^2$, this becomes:

$$\log(-\sigma_{ie}) - 0.868 \sinh^{-1}(9.05 \times 10^7 \sigma_{ie}) - \log(2 \times 10^{-6} - |\sigma_{ie}|) = pH - pK_{a2}^{int} \quad (11-74)$$

In the cases where pH is between pK_{a1}^{int} and pK_{a2}^{int} , both parts of the right-hand side of Eq. 11-69 must be evaluated.

In the special case near the oxide's pH_{zpc} where ψ is small (absolute value less than 25 mV) and with a low ionic strength, Eq. 11-68 becomes:

$$\psi = \frac{2.303 RT}{F} (pH_{zpc} - pH) \quad (11-75)$$

and we may estimate the solid's surface charge density:

$$\sigma_{ie} = [6.40 \times 10^{-10} (T \cdot I \cdot 10^3)^{0.5}] \sinh [1.15 z (pH_{zpc} - pH)] \quad (11-76)$$

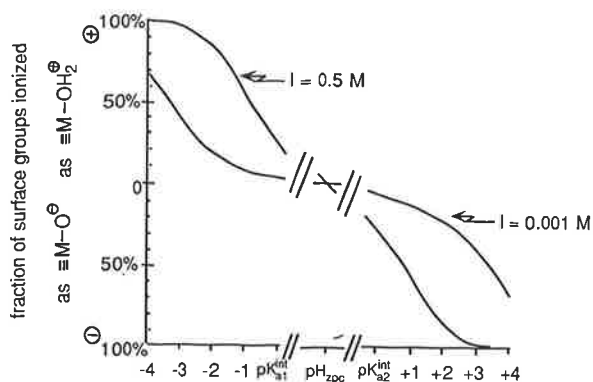


Figure 11.19 Variation of surface charge on a solid oxide (25°C) due to protonation and deprotonation of surface hydroxyls (at $2 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$) as a function of solution pH for (a) $I = 0.5 \text{ M}$ of a dissolved salt with both the cation and the anion exhibiting one charge (1:1 electrolyte) and (b) $I = 0.001 \text{ M}$ 1:1 electrolyte. Note the breaks in the curves between unspecified values of pK_{a1}^{int} and pK_{a2}^{int} .

intrinsic acidity constants. Typically, surface charge densities in the range of 10^{-6} to $10^{-8} \text{ mol} \cdot \text{m}^{-2}$ are seen for oxides, and this implies that 10^{-6} – 10^{-8} moles of counterions, including some charged organic molecules, will accumulate opposite each meter squared of surface area due to electrostatic attractions. This property of surfaces is sometimes referred to as the oxide's cation exchange capacity (CEC) or anion exchange capacity (AEC). Note again, this treatment neglects the influence of specifically sorbed ions which would neutralize some of this surface charge [e.g., $\text{Fe}(\text{OH})_2^+$ bound in Region I of Fig. 11.18].

Clay minerals present a different case with regard to assessing their surface charge. These mixed aluminum oxides and silicon oxides (thus aluminosilicates) expose two kinds of surface to the external media, and therefore the same particles may exhibit both a CEC and an AEC at the same time (Table 11.5). First, the edges of these flakey-shaped minerals are somewhat like aluminum oxides in their behavior and respond to pH changes in solution much like pure aluminum oxides (e.g., pH_{zpc} of kaolinite edge ~ 7 , Williams and Williams, 1978). The consequent anion exchange capacity observed empirically for clays is near $1 \times 10^{-2} \text{ mole}/100 \text{ g}$ for a wide variety of clays (Grim, 1968), but this value changes with solution pH and ionic strength. On the other hand, the faces of these platey particles have a "siloxane" structure ($-\text{Si}-\text{O}-\text{Si}-$) which does not leave any free hydroxyl groups ($-\text{Si}-\text{OH}$) to participate in proton exchange reactions with the bulk solution. Instead, the faces exhibit a charge due to cation substitutions for the aluminum or silicon atoms within the internal structure. These "isomorphic" substitutions often involve cations of lower total positive charge (e.g., Al^{+3} for Si^{+4} or Mg^{+2} for Al^{+3}). The result is a fixed and permanent charge deficiency that looks like a negative surface charge to the surrounding solution. Empirical measures of this negative surface charge or CEC are

TABLE 11.5 Sorbent Properties of "Pure Solids" Commonly Present in Aquatic Environments^a

TABLE 11.5 Sorbent Properties of "Pure Solids" Commonly Present in Aquatic Environments

Sorbent	Category		Specific Surface Area (m ² ·g ⁻¹)	CEC (mol·m ⁻²)	AEC (mol·m ⁻²)	pK _{a1} ^{int}	pK _{a2} ^{int}	pH _{zpc}	Ref. ^b
	Compositions								
Oxides									
Quartz	SiO ₂		0.14	9 × 10 ^{-8*}		(-3)	7	2.0	1,2
Amorphous silica	SiO ₂		500	9 × 10 ^{-8*}		(-3)	7	2.0	1,2
Goethite	α-FeOOH		46		2 × 10 ^{-8*}	6	9	7.5	2
Amorphous iron oxide	Fe(OH) ₃		600		5 × 10 ^{-8*}	7	9	8	2,4,5
Alumina	Al ₂ O ₃		15		8 × 10 ^{-8*}	7	10	8.5	2
Gibbsite	Al(OH) ₃		120	2 × 10 ^{-8*}		5	8	6.5	2,6
Aluminosilicates									
Na-montmorillonite	Na ₃ Al ₇ Si ₁₁ O ₃₀ (OH) ₆		600-800	0.9 to 2 × 10 ⁻⁶	3 to 4 × 10 ⁻⁷			2.5	6,7
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄		12	0.2 to 1 × 10 ⁻⁵	0.6 to 2 × 10 ⁻⁵			4.6	
Illite	KAl ₃ Si ₃ O ₁₀ (OH) ₂		65-100	1 to 6 × 10 ⁻⁶	3 × 10 ⁻⁷				
Organic									
Humus	C ₁₀ H ₁₂ N _{0.4} O ₆		1	1 to 10 × 10 ⁻³					8,9
Carbonate									
Calcite	CaCO ₃		1		9 × 10 ⁻⁶			8-9.5	10,11

^aCalculated CEC and AEC values (*) assume solution pH = 7, ionic strength of 10⁻³ M, T = 293 K, solid-site density of 2 × 10⁻⁶ mol·m⁻², and use of Eq. 11-69 or 11-76. Intrinsic acidity constants are rounded off to the nearest unit.

^bReferences: 1. Parks (1965), 2. Schindler and Stumm (1987), 3. Mikhail et al. (1968a, b), 4. Tipping (1981), 5. Dzombak and Morel (1990), 6. Davis (1982), 7. Grim (1968) 8. Chiou et al. (1990), 9. Khan (1980), 10. Zullig and Morse (1988), 11. Somasundaran and Agar (1967).

made by assessing the maximum concentrations of weakly bound cations such as ammonium, NH_4^+ , that can be sorbed. Table 11.5 shows the results of such cation exchange capacity tests on three common clays, montmorillonite, illite, and kaolinite. Expandable three-layer clays like montmorillonite exhibit the highest CEC's near 1×10^{-1} mol/100 g (Grim, 1968) or 1.4×10^{-6} moles of charged sites per meter squared (assuming a specific surface area of $700 \text{ m}^2/\text{g}$). On the other extreme, two-layer kaolinite clays exhibit the lowest CEC's of about 1×10^{-2} mol/100 g (Grim, 1968). This is chiefly due to their greatly reduced specific surface areas compared to the expandable three-layer clays, since per unit area these kaolinites actually have greater charge density, $\sim 10^{-5} \text{ mol/m}^2$.

Particulate natural organic matter may also contribute to the assemblage of charged sites of solids in water. This is mostly due to ionization reactions of carboxyl groups ($-\text{COOH}$), and at higher pH values, phenolic groups (aromatic ring $-\text{OH}$), which have been found at about 1–10 mM per gram of natural organic matter. Depending on the surrounding molecular environment, the carboxyl moieties exhibit pK_a 's ranging from about 3 to 6. Consequently, the extent of charge buildup in the organic portion of natural particles will vary as a function of pH.

Still other solid phases, like carbonates, are common in nature, and these materials also exhibit surface charging. Realizing there will almost always be charges on particle surfaces submerged in water, we can now examine their impact with regard to sorbing ionized organic chemicals from solution.

Sorption of Organic Counterions to Single Solids by Ion Exchange Mechanisms

Let us now proceed to examine the quantities of organic ions that associate through ion exchange with a single type of solid surface in aqueous solution. For example, we consider the case of adding ethyl ammonium chloride ($\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$; pK_a of the alkyl ammonium ~ 10) to a 10^{-2} M NaCl solution at pH 6 which also contains suspended montmorillonite particles. We do not need to consider ammonium ion ($\text{CH}_3\text{CH}_2\text{NH}_3^+$) bond formation with the clay surface, nor must we be concerned with neutral amine absorption into particulate organic matter in this case, since we have chosen solids which lack this phase. Consequently, the solid–water distribution coefficient involves only

$$K_d(\text{ethyl amine plus ethyl ammonium ions}) = \frac{[\text{ethyl ammonium ions near clay surface}]}{[\text{ethyl ammonium ions in solution}]} \quad (11-77)$$

at pH's (i.e., < 8) where we can assume that the positively charged species is much more abundant than its neutral conjugate base both in solution and near the clay surface. Before we added any alkyl ammonium salt, the negative surface charges of the clay were balanced by an excess of hydrated sodium cations relative to hydrated chloride ions accumulated in the thin film of water surrounding the particles (Fig. 11.18). When we add a small quantity of the alkyl ammonium salt to the suspension (insufficient to change the ionic strength), an ion exchange reaction occurs

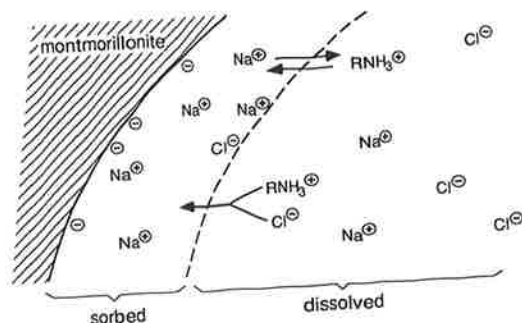
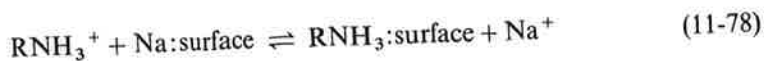


Figure 11.20 Illustration of two types of transfer enabling organic ammonium ions to collect near a negatively charged solid surface: exchange with Na^+ or cotransfer with Cl^- .

(Fig. 11.20):



resulting in some of the ammonium ions exchanging with Na^+ counterions in Region II near the solid's surface (the colon here indicates association without bond formation and $\text{R} = \text{CH}_3\text{CH}_2$). We can write an equilibrium constant expression for this ion exchange reaction:

$$K_{ie} = \frac{[\text{RNH}_3:\text{surface}][\text{Na}^+]}{[\text{RNH}_3^+][\text{Na}:\text{surface}]} \quad (11-79)$$

where we have used concentrations in place of activities. (A complete equilibrium expression would include activity coefficients for the charged species; however, since this equation involves monovalent ions both in the bulk medium and near the surface, such activity coefficients virtually cancel one another out in the equilibrium quotient.) K_{ie} reflects the preference of organic sorbate relative to the competing sorbates, in this case Na^+ . Recognizing that the accumulation of counterion cations around the negatively charged particles must be a constant equal to the product of the surface charge density σ_{ie} ($\text{mol} \cdot \text{m}^{-2}$) and the specific particle surface area A ($\text{m}^2 \cdot \text{kg}^{-1}$), we can write

$$\sigma_{ie} \cdot A = [\text{RNH}_3:\text{surface}] + [\text{Na}:\text{surface}] \quad (11-80)$$

where $[\text{RNH}_3:\text{surface}]$ and $[\text{Na}:\text{surface}]$ have units of moles per kilogram. We can now eliminate the term in $[\text{Na}:\text{surface}]$ from the equilibrium constant expression 11-79:

$$K_{ie} = \frac{[\text{RNH}_3:\text{surface}][\text{Na}^+]}{[\text{RNH}_3^+](\sigma_{ie} \cdot A - [\text{RNH}_3:\text{surface}])} \quad (11-81)$$

Rearranging this expression, we find

$$[\text{RNH}_3^+ \text{ : surface}] = \frac{(\sigma_{\text{ie}} \cdot A)(K_{\text{ie}})[\text{RNH}_3^+]}{[\text{Na}^+] + (K_{\text{ie}})[\text{RNH}_3^+]} \quad (11-82)$$

or more generally,

$$\left[\begin{array}{c} \text{organic ion} \\ \text{at surface} \end{array} \right] = \frac{\sigma_{\text{ie}} \cdot A \cdot K_{\text{ie}}[\text{organic ion in solution}]}{[\text{competing ion}] + K_{\text{ie}}[\text{organic ion in solution}]} \quad (11-83)$$

In terms of the particular example at hand, Eq. 11-82 says that the concentration of bound alkyl ammonium ion varies as we change the concentration of the dissolved species (Fig. 11-21a). At low organic ion concentrations ($[\text{Na}^+] \gg K_{\text{ie}}[\text{RNH}_3^+]$), the bound-to-dissolved *ratio* is almost constant:

$$K_d \simeq \left(\frac{\text{total net}}{\text{surface charge}} \right) \cdot \left(\frac{\text{equilibrium}}{\text{constant}} \right) \cdot \left(\frac{\text{competing cation}}{\text{concentration}} \right)^{-1} \quad (11-84)$$

On the other hand, at high levels of RNH_3^+ , the bound counterion concentrations asymptotically approach a constant value set by the total surface charge density (in this case, the cation exchange capacity of the clay). At these elevated charged organic sorbate levels, the bound-versus-dissolved distribution ratio actually declines, and the isotherm is hyperbolic (Fig. 11-21a). An isotherm having this shape is generally referred to as a *Langmuir isotherm*:

$$[\text{Sorbed}] = \frac{[\text{maximum sorbed}] K_{\text{Langmuir}}[\text{dissolved}]}{1 + K_{\text{Langmuir}}[\text{dissolved}]} \quad (11-85)$$

where in this case $[\text{maximum sorbed}] = \sigma_{\text{ie}} \cdot A$, and $K_{\text{Langmuir}} = K_{\text{ie}}/[\text{competing ion}]$.

We can confirm the direct relationship (expected from Eq. 11-84) of the bound-to-dissolved distribution ratio with the surface charge density for low concentrations of organic sorbate ions by examining the results of Fuerstenau and Wakamatsu (1975). In this case, alumina was used as a positively charged sorbent ($\text{pH}_{\text{zpc}} \simeq 8.5$) and dodecylsulfonate anions were exchanged with background chloride ions for ion exchange sites on this solid as a function of solution pH. (Alkyl sulfonates, $\text{R}-\text{SO}_3^-$, do not appear to participate in substantial ligand exchange reactions with alumina.) Based on Eq. 11-69, we calculate how the alumina's surface charge density σ should have decreased with increasing pH (Fig. 11-22a). Using these results, we anticipate that $K_d(\text{dodecylsulfonate}) \cdot A^{-1}$ should be lowest at high pH when σ is lowest, and this is exactly what these workers observed (Fig. 11-22b). The direct correlation of these observed ($K_d \cdot A^{-1}$)'s with the calculated σ_{ie} 's yields a slope which, when adjusted by the competing chloride concentration, suggests K_{ie} is between 20 and 50. This implies the dodecylsulfonate was accumulated in the diffuse double layer surrounding the alumina relative to its bulk solution concentration more than an order of

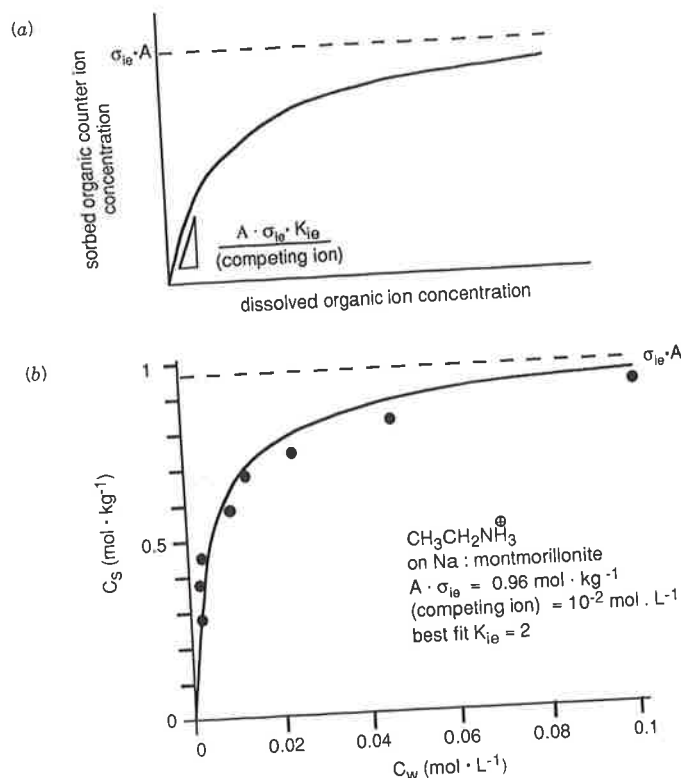


Figure 11.21 (a) Schematic Langmuir isotherm showing the variation of sorbed organic counterions (i.e., those within the near surface water layer) as dissolved (or bulk solution) organic ion concentration changes: $\sigma_{ie} \cdot A$ is the total surface charge density; K_{ie} is the exchange reaction equilibrium constant; and (competing ion) is the concentration of competing counterions. (b) For the specific case of ethyl ammonium sorption to montmorillonite, a Langmuir isotherm with best fit $K_{ie} = 2$ matches the experimental data well (data from Cowan and White, 1958).

magnitude more preferentially than the inorganic chloride adsorbate ($\Delta G_{\text{ads}} \approx 7\text{--}10 \text{ kJ} \cdot \text{mol}^{-1}$). These findings clearly illustrate the direct effect of the particle's surface charge density on the extent of adsorption of organic counterions. We should note that at the point where $[\text{organic ion}] \approx [\text{competing ion}]$, further increases in $[\text{organic ion}]$ cause substantial changes in the solution ionic strength. Were we considering an oxide surface, such an important change in the solution would result in a concomitant slow increase in the surface charge (recall Eq. 11-68 in Table 11.4). Obviously, this effect on σ_{ie} would feed back into the extent of sorption.

Now let's examine the effectiveness of such a modeling approach for ethyl

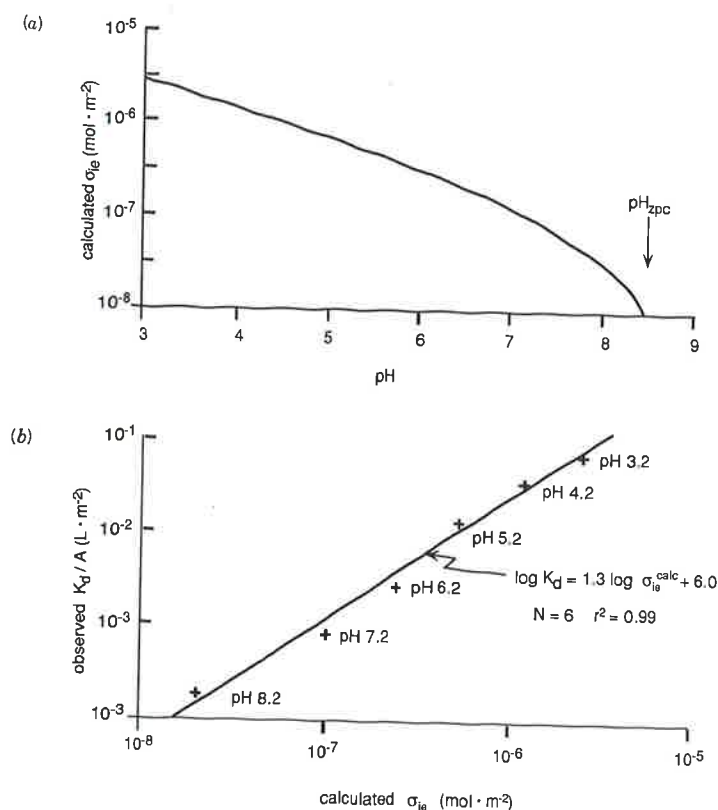


Figure 11.22 (a) Expected variation of the surface charge density σ_{ie} of alumina as a function of pH ($I = 2 \times 10^{-3} \text{ M}$, $T = 25^\circ \text{ C}$, $[\equiv \text{MOH}]_0 = 5 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2}$). (b) Direct relationship between observed sorption of dodecyl sulfonate on alumina (Fuerstenau and Wakamatsu, 1975) and calculated σ_{ie} .

ammonium sorption to a Na-montmorillonite (Cowan and White, 1958). These workers measured the CEC ($= \sigma_{ie} \cdot A$) of their clay sorbent to be nearly $1 \text{ mol} \cdot \text{kg}^{-1}$ (recall that this surface charge is not sensitive to solution ionic strength like the oxides, since it arises principally from isomorphic substitutions). Working with $[\text{Na}^+] = 10^{-2} \text{ M}$, the observed isotherm data can be nicely fit with $K_{ie} = 2$ (Fig. 11-21b). Since $K_{ie} = 1$ would imply no preference between the sodium and the alkyl ammonium ions, this fit value of K_{ie} indicates only a little selection of the organic cation over the sodium ion, presumably because of the hydrophobicity of the ethyl substituent. We also deduce that for ethyl ammonium concentrations less than about 10^{-2} M (i.e., less than the Na^+ concentration) we have a constant K_d (ethyl ammonium ion) of about $200 (\text{mol} \cdot \text{kg}^{-1})(\text{mol} \cdot \text{L}^{-1})^{-1}$ [$= \sigma_{ie} \cdot A \cdot K_{ie}(\text{competing ion})^{-1} = \text{CEC} \cdot K_{ie} \cdot [\text{Na}^+]^{-1}$]. Obviously, solutions of lower competing cation concentrations would allow the sorbed-to-dissolved ratio to be even greater. Given the ionic strength of 10^{-2} M ,

we recognize the characteristic length of the diffuse double layer is about 3 nm; together with an estimate of this montmorillonite's surface area ($\sim 700 \text{ m}^2/\text{g}$), we can calculate that this distribution ratio corresponds to about $60 (\text{mol} \cdot \text{L}^{-1} \text{ double layer water}) \cdot (\text{mol} \cdot \text{L}^{-1} \text{ bulk water})^{-1}$. Clearly, the electrostatic attraction of the negatively charged clay faces is concentrating cations like ethyl ammonium ions in the water near the particles. In addition, as also indicated by the dodecylsulfonate sorption to alumina, we recognize that the rest of the organic structure (R) plays a role in determining the magnitude of K_{ie} .

Effects of Sorbate Hydrophobicity Thus our problem involves the question of how various hydrophobic portions of charged organic sorbates influence their sorption. Presumably the sorbate's chemical structure determines the preference of the sorbate for the near-particle water region versus the bulk solution. Cowan and White (1958) investigated the sorption of a series of alkyl ammonium ions to the same Na-montmorillonite (Fig. 11-23). A very interesting pattern emerged: *the longer the alkyl chain, the steeper was the initial isotherm slope*. Exactly parallel results have been seen for sorption of other amphiphiles, for example, negatively charged *n*-alkyl benzene sulfonates binding to positively charged alumina particles (Somasundaran et al., 1984). Further, *above about eight carbons in the chain, the extent of binding*

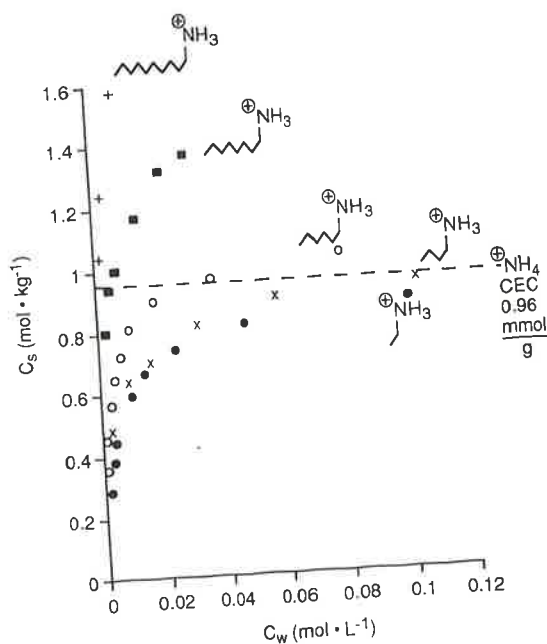


Figure 11.23 Adsorption isotherms for a series of alkyl ammonium compounds on sodium montmorillonite (adapted from Cowan and White, 1958). The horizontal dashed line indicates the cation exchange capacity of the clay.

could far exceed the clay's cation exchange capacity. Using quartz as a sorbent, Somasundaran et al. (1964) showed that chain lengths of about 10 carbons or more in alkyl ammonium ions could bind to the particles enough to reverse the particles' surface charge (i.e., convert negatively charged particles to positively charged ones by including counterions within what we called Region I in Fig. 11.18). These effects are undoubtedly due to the increasing hydrophobicity of the longer and longer chains. By favoring chemical partitioning to the near surface (e.g., into near surface water as we saw in Section 11.5) from the bulk solution, hydrophobic forces augment the electrostatic forces and thereby enhance the tendency of the sorbates to collect near the particle surface (Somasundaran et al., 1984). Thus, we anticipate little differences in sorption for organic chemicals due to moieties of like charge (e.g., $-\text{COO}^-$ vs. $-\text{SO}_3^-$), since the electrostatic attraction to a surface is fairly nonselective; but we do expect substantial variations between sorbates if they differ in the hydrophobicity of their nonpolar parts (analogous to Eq. 11-40 for neutral sorbates associating with minerals).

To provide an estimate of K_{ie} suitable for use in Eq. 11-83, let us try to isolate the contribution of the sorbate's hydrophobicity using some available data. First, recalling the ion exchange equilibrium expression,

$$K_{ie} = \frac{[\text{RNH}_3:\text{surface}][\text{Na}^+]}{[\text{RNH}_3^+][\text{Na}:\text{surface}]} \quad (11-79)$$

we see that this can be considered to consist of two individual partitioning processes, one for RNH_3^+ and the other for Na^+ . Each of these species finds itself distributed between the bulk solution and the near-surface environment according to the respective free energy differences. For the sodium ion, this free energy difference consists of only an electrostatic contribution. The solid-water ratio is therefore given by

$$\begin{aligned} \frac{[\text{Na}:\text{surface}]}{[\text{Na}^+]} &= \exp(-\Delta G_{\text{elec}}/RT) \\ &= \exp(-zF\psi/RT) \end{aligned} \quad (11-86)$$

In contrast, the alkyl ammonium ions are driven to the surface, not only by electrostatic forcing, but also by a hydrophobic effect:

$$\begin{aligned} \frac{[\text{RNH}_3:\text{surface}]}{[\text{RNH}_3^+]} &= \exp [(-\Delta G_{\text{elec}} - \Delta G_{\text{hydrophob}})/RT] \\ &= \exp [(-zF\psi - \Delta G_{\text{hydrophob}})/RT] \end{aligned} \quad (11-87)$$

Here we assume that the Na^+ and the RNH_3^+ ions experience the same electrostatic attractions to the surface, although we know that factors like differences in solvation

have some effect. Substituting Eqs. 11-86 and 11-87 into Eq. 11-79 yields

$$K_{ic} = \exp [(-zF\psi - \Delta G_{\text{hydrophob}})/RT] / \exp (-zF\psi/RT) \quad (11-88)$$

$$= \exp (-\Delta G_{\text{hydrophob}}/RT)$$

Equation 11-88 indicates that the preference in ion exchange for organic ions over inorganic ones of the same valency (i.e., $z = 1$ for both sorbates) is mostly due to factors directing the organic sorbate to escape solution in bulk water. If we could evaluate this $\Delta G_{\text{hydrophob}}$ as a function of chemical structure, we could estimate K_{ic} for various organic sorbates competing with inorganic ions that do not bond with the surface.

Since this hydrophobic effect appears to regularly increase with the size of the nonpolar part of the chemical structure (Cowan and White, 1958; Somasundaran et al., 1984), we may reasonably propose this energy term is composed of contributions from each of the nonpolar parts of the structure. Consequently, we expect for the alkyl ammonium ions studied by Cowan and White (1958),

$$\Delta G_{\text{hydrophob}} = m \cdot \Delta G_{-\text{CH}_2-} \quad (11-89)$$

where m is the number of methylene ($-\text{CH}_2-$) groups in each sorbate's alkyl chain, and $\Delta G_{-\text{CH}_2-}$ is the hydrophobic contribution made by each methylene driving these sorbates into the diffuse double layer-vicinal water layer.

Thus, the total free energies directing these organic ions to distribute between the montmorillonite surface region and the bulk water would be

$$\Delta G_{\text{ads}} = -RT \ln(K_d \text{ of } \text{RNH}_3^+) = -RT \ln \left(\frac{[\text{RNH}_3^+ : \text{surface}]}{[\text{RNH}_3^+]} \right) \quad (11-90)$$

$$= zF\psi + m \cdot \Delta G_{-\text{CH}_2-}$$

Figure 11-24 shows the variation in ΔG_{ads} for these alkyl ammonium ions (when these organic sorbates are present at levels much less than Na^+) as a function of the number of methylenes in the alkyl chains. The least-squares correlation line through the data yields

$$\Delta G_{\text{ads}} = -10.9 - m \cdot 0.75 \quad (\text{kJ} \cdot \text{mol}^{-1}) \quad (11-91)$$

This result implies that the alkyl ammonium ions experienced an electrostatic attraction to the clay surface corresponding to

$$zF\psi \approx -10.9 \text{ kJ} \cdot \text{mol}^{-1} \quad (11-92)$$

or that $\psi \approx -0.11 \text{ V}$. Also, we see $\Delta G_{-\text{CH}_2-} = -0.75 \text{ kJ} \cdot \text{mol}^{-1}$. Examination of the variation in aqueous solubilities for compound classes like alkanes or alcohols

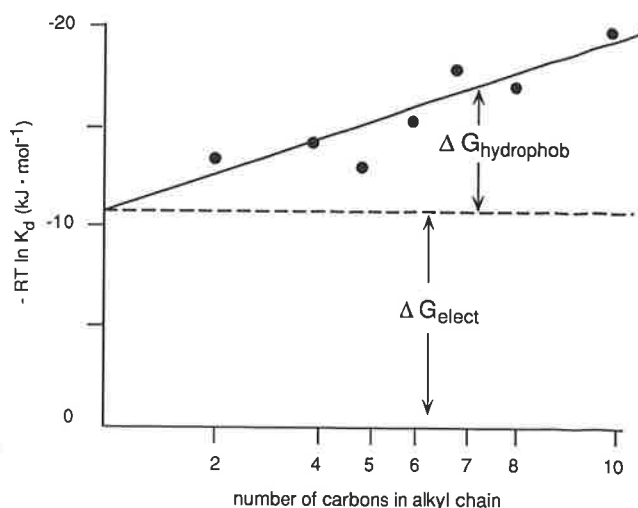


Figure 11.24 Variation in observed ion exchange free energy change ($-RT \ln K_d$) for a series of alkyl ammonium ions associating with a sodium montmorillonite. All K_d 's taken at low organic ion concentrations. The least-squares fit line yields an intercept of $-10.9 \text{ kJ} \cdot \text{mol}^{-1}$ and a slope of $0.75 \text{ kJ} \cdot \text{mol}^{-1}$ per methylene group (data from Cowan and White, 1958).

(Chapter 5) as a function of additional methylene groups reveals that ΔG_s^e changes by almost $4 \text{ kJ} \cdot \text{mol}^{-1}$ for each increase in chain length. Thus, the $\Delta G_{-\text{CH}_2-}$ contributing to ΔG_{ads} in Eq. 11-91 corresponds to "a relief" of about 20% of the excess free energy of aqueous solution per methylene group. Somasundaran et al. (1984) noted that inclusion of the phenyl group in alkyl aryl sulfonates increases the ion exchange sorption tendency of these amphiphiles to a degree corresponding to lengthening the alkyl chain by 3–4 methylene groups. This is consistent with increasing the nonpolar structure's hydrophobicity to the same extent [i.e., $\Delta \log K_{\text{ow}}(\text{phenyl}) \approx 1.68$ and $\Delta \log K_{\text{ow}}(3\text{--}4 \text{ methylenes}) \approx 1.59$ to 2.12]. Thus, we may be justified in estimating the hydrophobic contribution to K_{ie} for charged organic sorbates as a fraction, say 20%, of the excess free energy of aqueous solution in the corresponding hydrocarbon:

$$K_{\text{ie}} = \exp(-\Delta G_{\text{hydrophob}}/RT) \quad (11-88)$$

$$\approx \exp(+0.2\Delta G_s^e/RT) \quad (11-93)$$

$$\approx \exp\left(+0.2 \cdot \left(RT \ln \frac{55.3}{C_w^{\text{sat}}(l, L)}\right) / RT\right) \quad (11-94)$$

$$\approx 2.2[C_w^{\text{sat}}(l, L)]^{-0.2} \quad (11-95)$$

The data of Cowan and White (1958) yield the empirical result

$$K_{ie} = 1.1(C_w^{sat})^{-0.19} \quad (11-96)$$

using the solubilities of the corresponding alkanes. Such expressions predict that K_{ie} of decyl amine to be 19 (Eq. 11-96) or 45 (Eq. 11-95), since $10^{-6.57}$ M is the liquid solubility of decane. Cowan and White (1958) observed $K_{ie}(\text{decyl amine})$ to be 36. There is little doubt that hydrophobic phenomena are playing a role in determining the extent of amphiphilic sorption; however, a great deal more work is necessary before approaches such as Eq. 11-95 or 11-96 are proven to be robust.

Multisite, Multimechanism Sorption Because the sorbed concentration can exceed $\sigma_{ie} \cdot A$ (Fig. 11-23), and the observation that real-world sorbents are not well fit with a single Langmuir isotherm (Fig. 11-25), we must consider other sorptive mechanisms in addition to the ion exchange one portrayed in Eq. 11-78. For example, recognizing the need to maintain electroneutrality near the solid's surface, a second exchange process has been postulated (Brownawell et al., 1990), which for our alkyl ammonium case would look like

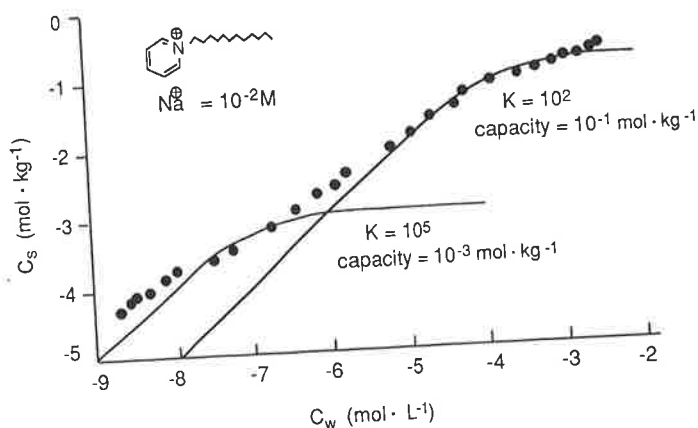
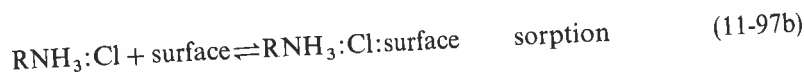
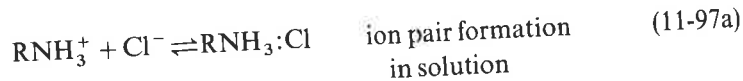


Figure 11.25 Observed sorption of dodecylpyridinium on a soil (EPA-12) exhibiting an overall cation exchange capacity of $0.135 \text{ mol} \cdot \text{kg}^{-1}$. Two Langmuir isotherms are placed on the data to illustrate how different portions of the observed isotherm may reflect the influence of different materials in the complex soil sorbent or possibly different mechanisms (data from Brownawell et al., 1990).

We note especially that *the surface need not be charged to act as a sorbent in this process*. The physical picture associated with Eqs. 11-97a and 11-97b is that the organic ion with a companion (inorganic) counterion form an ion pair and moves together into the layer of water near the particle surface (Fig. 11-20). Presumably this transfer occurs because the hydrophobic portion of the organic ion has some desire to escape the bulk water and move into the near surface water. The equilibrium expression for this *non-ion exchange* process is

$$K_{nie} = \frac{[\text{RNH}_3:\text{Cl:surface}]}{[\text{RNH}_3^+][\text{Cl}^-][\text{surface}]} \quad (11-98)$$

where we include the activity coefficients applicable to charged species in K_{nie} . Similar to the ion exchange mechanism, this electroneutral sorption is ultimately limited by the capacity of the solid surface available to sorb the amphiphile. Thus we may write

$$\begin{aligned} \text{Total capacity} &= [\text{RNH}_3:\text{Cl:surface}] + [\text{surface}] \\ &= A/a \end{aligned} \quad (11-99)$$

where a is the surface area "covered" by a mole of sorbate molecules ($\text{m}^2 \cdot \text{mol}^{-1}$) and A is the total available surface area of the solids ($\text{m}^2 \cdot \text{kg}^{-1}$).

Substituting Eq. 11-99 into Eq. 11-98, we have

$$K_{nie} = \frac{[\text{RNH}_3:\text{Cl:surface}]}{[\text{RNH}_3^+][\text{Cl}^-](A/a - [\text{RNH}_3:\text{Cl:surface}])} \quad (11-100)$$

which, upon rearrangement, yields a second Langmuir isotherm:

$$[\text{RNH}_3:\text{Cl:surface}] = \frac{A/a \cdot K_{nie} \cdot [\text{RNH}_3^+]}{[\text{Cl}^-]^{-1} + K_{nie}[\text{RNH}_3^+]} \quad (11-101)$$

For this mechanism, the maximum sorbed concentration is given by A/a (mole per kilogram) and K_{Langmuir} is equal to $K_{nie} \cdot [\text{companion counterion}]$.

Now we can see how the sorbed concentration can exceed the cation (or anion) exchange capacity for amphiphilic sorbates if we assume K_{nie} values (Fig. 11.26). The total sorption process involves both ion exchange and non-ion exchange mechanisms operating simultaneously (i.e., the cations shown in Eqs. 11-78 and 11.97; Fig. 11.20). The solid-water distribution coefficient can be deduced by summing the two contributions:

$$\begin{aligned} [\text{RNH}_3 \text{ sorbed}] &= [\text{RNH}_3:\text{surface}] + [\text{RNH}_3:\text{Cl:surface}] \\ &= \frac{\sigma_{ie} \cdot A \cdot K_{ie} [\text{RNH}_3^+]}{[\text{Na}^+] + K_{ie} [\text{RNH}_3^+]} + \frac{A \cdot a^{-1} \cdot K_{nie} + [\text{RNH}_3^+]}{[\text{Cl}^-] + K_{nie} [\text{RNH}_3^+]} \end{aligned} \quad (11-102)$$

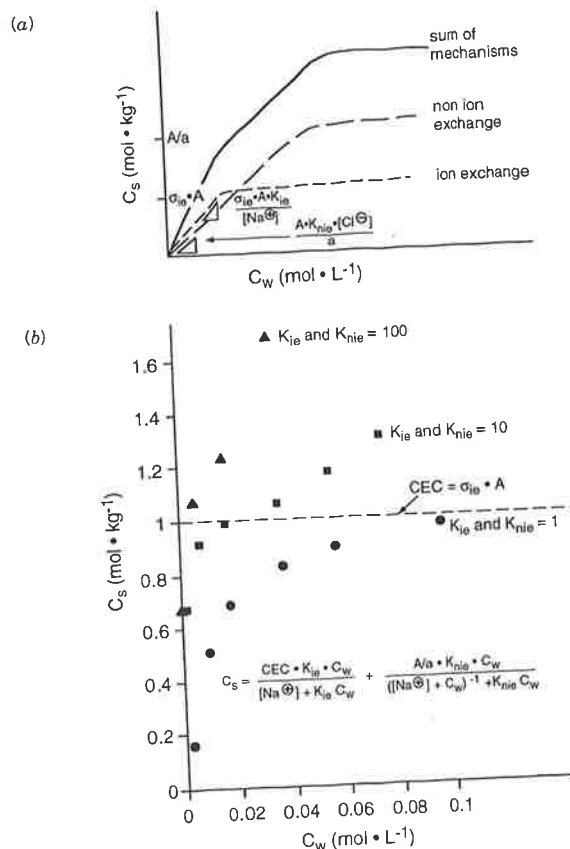


Figure 11.26 (a) Schematized isotherm for combination of ion exchange and nonion exchange mechanisms acting together; assumes $A/a > A \cdot \sigma_{ie}$ and $K_{ie} \cdot [\text{Na}^+]^{-1} > K_{nie} \cdot [\text{Cl}^-]$. (b) Calculated data points for specific cases where $K_{nie} = K_{ie}$, $\sigma_{ie} \cdot A = 1 \text{ mol} \cdot \text{kg}^{-1}$, $A/a = 4 \text{ mol} \cdot \text{kg}^{-1}$, $[\text{Na}^+] = 10^{-2} \text{ M}$, and $[\text{Cl}^-] = [\text{Na}^+] + [\text{R}^+]$. Note that $C_w = [\text{RNH}_3^+]$ and $C_s = [\text{RNH}_3^+ \text{ surface}] + [\text{RNH}_3^+ \text{Cl: surface}]$.

The combined isotherm appears as a somewhat "nonsharp" hyperbola, exhibiting a linear portion at sufficiently low dissolved sorbate concentrations and a plateau at suitably high levels (Fig. 11.26a). At intermediate concentrations, a gradual transition results from the differential maximization of the two sorption mechanisms. Depending on the magnitudes of K_{ie} and K_{nie} , various isotherms ranging from those looking like Langmuir (when one mechanism dominates) to Freundlich relations (when both mechanisms contribute) can be found (Fig. 11.26b). Obviously, the shape of the isotherm an experimentalist would see depends on the range of dissolved concentrations utilized. Nonetheless, the calculated isotherm points shown in Fig. 11.26b look remarkably like the measured data seen by Cowan and White (1958) for the several alkyl ammoniums they tested on a single sorbent (Fig. 11.23b).

Recent work (Brownawell et al., 1990) performed using soils and subsoils and examining dissolved concentrations spanning several orders of magnitude, suggests the heterogeneity of the natural sorbents is very important. It appears that, in addition to multiple sorption mechanisms acting simultaneously, one sees the influence of more than one solid surface type. Thus, the data require fits using several Langmuir isotherms, some for ion exchange interactions and possibly others for the non-ion exchange mechanism, but presumably each reflecting the involvement of different solid materials that make up the complex medium we simply call a soil, subsoil, or sediment.

Hemimicelles We conclude this discussion of amphiphilic sorption by discussing a special phenomenon called hemimicelle formation (Fuerstenau, 1956; Somasundaran et al., 1964; Chandar et al., 1983, 1987). This hemimicelle formation plays a critical role in amphiphile "sorption" to minerals when the organic ions are present at relatively high dissolved concentrations [about 0.001–0.01 of their critical micelle concentrations (CMC), i.e., the level at which they self-associate in the bulk solution]. When the organic sorbate levels are low, the sorption mechanism is like the ion exchange mechanism we discussed above (Fig. 11.27, I). At some point in a titration of sorbents by micelle-forming compounds, presumably due to both electrostatic and hydrophobic effects, amphiphile concentrations build up in the near-particle region to a point where it seems likely that self-aggregation of the molecules occurs in that thin water layer (Fig. 11.27, IIa). This in turn would allow the rapid coagulation of the aggregated amphiphiles with the oppositely charged particle surface, smothering that subarea of the particle's surface charge with what have been called hemimicelles (Fig. 11.27, IIb). Electrophoretic mobility measurements clearly demonstrate the neutralization of the particle's charges in this steep portion of the isotherm, even going so far as to reverse the surface charge (e.g., Chander et al., 1987). The onset of this particle coating by hemimicelles occurs at different dissolved concentrations for various amphiphiles, but is near millimolar levels (≥ 100 mg/L) for decyl-substituted amphiphiles and is near micromolar levels (≥ 100 μ g/L) for octadecyl derivatives. In all cases, the bulk solution concentration is much less than the CMC. It appears that the elevated near-surface concentrations, derived from accumulation of these amphiphiles in the thin film of water near the particle surface by factors of 100 or more, is compensating just enough to achieve critical micelle concentrations in this near-surface water layer. Continued increase in amphiphile concentration results in the particle surface becoming increasingly coated by hemimicelles, apparently while the near-surface water maintains its concentration near that of the CMC (Fig. 11.27 II). Finally, the entire particle surface is covered with a bilayer of amphiphile molecules; the particle's surface charge is now that of the surfactant; and the addition of more amphiphile to the solution does not yield any higher sorbed loads (Fig. 11.27, III). This especially extensive degree of sorption may be the cause of macroscopic phenomena such as dispersion of coagulated colloids and particle flotation.

An Example: Calculation of K_d of a Charged Organic Chemical We conclude the discussion of sorption of charged organic sorbates by examining the situation for

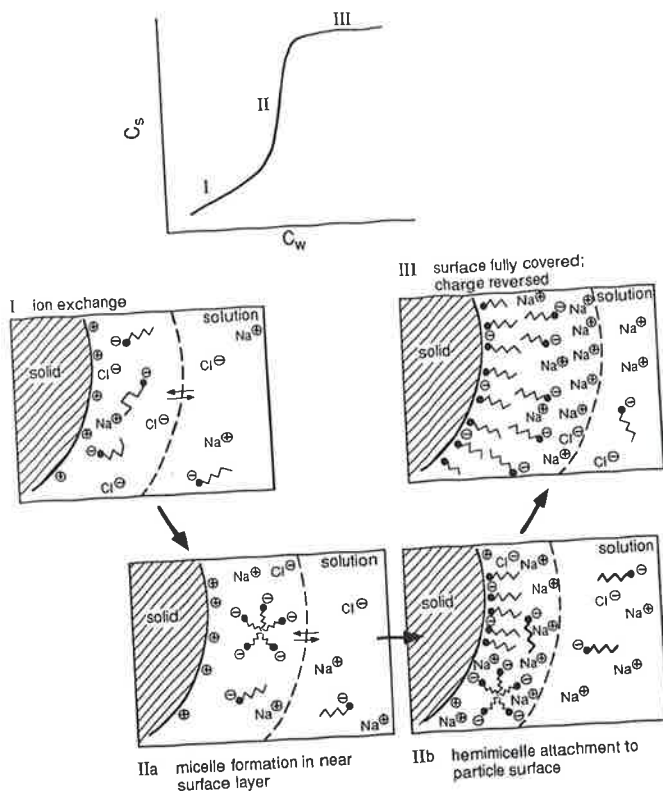


Figure 11.27 Relationship between sorbed and dissolved amphiphile concentration (upper isotherm plot). These different parts of the isotherm reflect changes in the solid surface as sorption proceeds, possibly explainable by the following: in portion (I) with low dissolved concentrations, sorption occurs via ion exchange and related mechanisms. At some point, sufficient near-surface concentration enhancement occurs that micelles form there (IIa) and rapid coagulation between oppositely charged micelles and the surface follows (IIb). When the surface becomes fully coated with such micelles, additional sorption is stopped (III). In portion II, the solid surface charge is converted from one sign to the other.

soils and sediments where both charged mineral surfaces and natural organic matter are present. The studies of Zachara et al. (1986) using quinoline as the sorbate are illustrative. This aromatic compound may occur in aqueous solution both as ionized



quinoline ($\log K_{ow} = 2.0$ for neutral species, $pK_a = 4.94$ for the protonated species)

and neutral species; thus we must consider simultaneous sorption of both. Recalling

Eq. 11-9, we may write for quinoline:

$$K_d = \frac{[Q]_{om} \cdot f_{om} + [QH^+]_{ie} \cdot \sigma_{ie} \cdot A}{[Q] + [QH^+]} \quad (11-103)$$

where

$[Q]_{om}$ is the concentration of quinoline associated with the natural organic matter,
 $[Q]_{ie}$ is the concentration of ionized quinoline opposite positions of negative charge on the solid surface,
 $[Q]$ is the concentration of the dissolved neutral quinoline species, and
 $[QH^+]$ is the concentration of the dissolved protonated quinoline species.

Here we assume sufficient f_{om} so that Q_{min} will be unimportant. We also assume that the structure of this substance does not enable Q_{rxn} to form. To simplify Eq. 11-103 we relate all species to the neutral dissolved concentration of quinoline, $[Q]$. First, using the acid-base equilibrium we express $[QH^+]$ as

$$[QH^+] = [Q][H^+](10^{+4.94}) \quad (\text{mol} \cdot \text{L}^{-1}) \quad (11-104)$$

Thus, information on solution pH will be necessary to calculate the fraction of quinoline present as charged molecules, and to evaluate the particle surface charge density σ_{ie} . Next, we can relate the concentration of neutral quinoline sorbed to natural organic matter to the dissolved neutral quinoline concentration via Eq. 11-15:

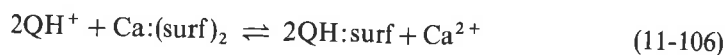
$$[Q]_{om} = K_{om} \cdot [Q] \quad (\text{mol} \cdot \text{kg}^{-1} \text{ om}) \quad (11-105)$$

On the whole-solid basis, this sorption to the natural organic matter contributes $f_{om} \cdot K_{om} \cdot [Q]$. Using a correlation expression such as that for aromatic hydrocarbons (Eq. 11-22a), we can estimate K_{om} using quinoline's octanol-water partition constant:

$$\begin{aligned} \log K_{om} &= 1.01(\log K_{ow}) - 0.72 \\ &= 1.01(2.0) - 0.72 \\ &= 1.3 \\ K_{om} &= 20 \end{aligned} \quad (11-22a)$$

Thus, we have for a soil of interest: $[Q_{om}] \approx f_{om} \cdot 20 \cdot [Q]$.

Finally, we must characterize QH^+ sorbed by ion exchange in terms of $[Q]$. For the particular studies of Zachara et al. (1986), the aqueous solution was maintained at 10^{-2} M CaCl_2 ; consequently, we consider the ion exchange reaction in which QH^+ replaces Ca^{2+} :



The ion exchange equilibrium expression for this reaction is

$$K_{ie}(\text{mol} \cdot \text{kg}^{-1}) \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} = \frac{[\text{QH:surf}]^2 [\text{Ca}^{2+}]}{[\text{QH}^+]^2 [\text{Ca:(surf)}_2]} \quad (11-107)$$

Note that the reaction stoichiometry gives us a K_{ie} expression somewhat different than that if Na^+ were the competing cation. To eliminate $[\text{Ca:(surf)}_2]$, we use the fact that the particle surface charge density must equal the accumulated concentrations of counterion sorbates:

$$A \cdot \sigma_{ie}(\text{mol} \cdot \text{kg}^{-1}) = [\text{QH:surf}] + 2[\text{Ca:(surf)}_2] \quad (11-108)$$

Using this charge balance equation in Eq. 11-107, we obtain

$$K_{ie} = \frac{[\text{QH:surf}]^2 [\text{Ca}^{2+}]}{[\text{QH}^+]^2 (0.5)(A \cdot \sigma_{ie} - [\text{QH:surf}])} \quad (11-109)$$

which on rearrangement yields

$$[\text{QH:surf}] = \frac{(0.5)K_{ie} \cdot \sigma_{ie} \cdot A \cdot [\text{QH}^+]^2}{[\text{QH:surf}][\text{Ca}^{2+}] + (0.5)K_{ie} \cdot [\text{QH}^+]^2} \quad (11-110)$$

We see a result which is similar to Eq. 11-82; but owing to the double charge of calcium ions, this expression is somewhat more complex. At very low concentrations of QH^+ we have $[\text{QH:surf}] \cdot [\text{Ca}^{2+}] \gg (0.5)K_{ie} \cdot [\text{QH}^+]^2$; thus, under these conditions the ratio of bound-to-dissolved QH^+ species is constant:

$$\frac{[\text{QH:surf}]}{[\text{QH}^+]} = \left[\frac{K_{ie} \cdot \sigma_{ie} \cdot A}{2[\text{Ca}^{2+}]} \right]^{0.5} \quad (11-111)$$

On the other hand, at high concentrations of QH^+ we see the sorbed species concentration asymptotically approaches $\sigma_{ie} \cdot A$.

We can also see how sorption via this ion exchange mechanism will be a function of pH. Using Eq. 11-104 to replace $[\text{QH}^+]$ in Eq. 11-110, we arrive at

$$[\text{QH:surf}] = \frac{(0.5)K_{ie}\sigma_{ie}A[\text{Q}]^2[\text{H}^+]^2(10^{+4.94})^2}{[\text{QH:surf}][\text{Ca}^{2+}] + (0.5)K_{ie}[\text{Q}]^2[\text{H}^+]^2(10^{+4.94})^2} \quad (11-112)$$

Or at low concentrations of Q , and hence QH^+ , we have

$$[\text{QH:surf}] = \left[\frac{K_{ie} \cdot \sigma_{ie} \cdot A}{2[\text{Ca}^{2+}]} \right]^{0.5} [\text{Q}][\text{H}^+](10^{+4.94}) \quad (11-113)$$

whereas at high concentrations of [Q] we still approach

$$[\text{QH}:\text{surf}] = \sigma_{\text{ie}} \cdot A$$

We also note for K_{ie} :

$$K_{\text{ie}} = \frac{[\text{QH}:\text{surf}]^2 [\text{Ca}^{2+}]}{[\text{QH}^+]^2 [\text{Ca}:\text{surf}_2]} \quad (11-107)$$

$$= \frac{K_{\text{d}}^2 \text{ of } \text{QH}^+}{K_{\text{d}} \text{ of } \text{Ca}^{2+}} \quad (11-114)$$

$$= \frac{(e^{-F\psi/RT} e^{-\Delta G_{\text{hydrophob}}/RT})^2}{(e^{-2F\psi/RT})} \quad (11-115)$$

$$\approx (e^{-2\Delta G_{\text{hydrophob}}/RT}) \quad (11-116)$$

This result implies that the exchange of two QH^+ for Ca^{2+} will favor the organic sorbate by an amount related to the *square* of the "desire" of the nonpolar portion of the molecule to escape the bulk water in favor of the near-particle-surface solution. As we saw earlier (Eqs. 11-88 to 11-96), this led us to relate K_{ie} to $[C_{\text{w}}^{\text{sat}}(1, L)]^{-0.2}$ of the comparable hydrocarbon making up the rest of the amphiphile's structure. Using naphthalene's subcooled liquid solubility ($10^{-3.06}$ M) to estimate quinoline's K_{ie} , we find that $[(10^{-3.06})^{-0.2}]^2 \approx 20$.

With these results, we can now rewrite the distribution coefficient expression 11-103 entirely in terms of Q for situations in which there are only low levels of this sorbate:

$$\begin{aligned} K_{\text{d}} &= \frac{f_{\text{om}} K_{\text{om}} [\text{Q}] + (K_{\text{ie}} \sigma_{\text{ie}} \cdot A / 2 [\text{Ca}^{2+}])^{1/2} ([\text{H}^+] / K_{\text{a}}) [\text{Q}]}{[\text{Q}] + ([\text{H}^+] / K_{\text{a}}) [\text{Q}]} \\ &= \frac{f_{\text{om}} K_{\text{om}} + (K_{\text{ie}} \sigma_{\text{ie}} \cdot A / 2 [\text{Ca}^{2+}])^{1/2} ([\text{H}^+] / K_{\text{a}})}{1 + ([\text{H}^+] / K_{\text{a}})} \end{aligned} \quad (11-117)$$

At high levels of $[\text{QH}^+]$ (relative to the competing cations), we have

$$K_{\text{d}} = \frac{f_{\text{om}} K_{\text{om}} [\text{Q}] + \sigma_{\text{ie}} \cdot A}{[\text{Q}] + ([\text{H}^+] / K_{\text{a}}) [\text{Q}]} \quad (11-118)$$

These mixed-sorption-mechanism K_{d} expressions now allow estimation of the overall extent of sorption in terms of compound properties (K_{om} , K_{ie} , K_{a}), particle properties (f_{om} , σ_{ie} , A), and solution properties ($[\text{Ca}^{2+}]$, pH). They also enable a side-by-side comparison of which species dominate in the particulate and dissolved phases.

Let us now use these results to estimate solid-solution distributions of quinoline.

Zachara et al. (1986) used a B horizon soil with $f_{om} \approx 0.0048$, $CEC \approx 8.4 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$, and 0.01 M CaCl_2 background electrolyte to examine quinoline sorption. Assuming the CEC was due to a substantial portion of clay (28% in the particle size distribution), we expect that this parameter is not sensitive to solution pH. To estimate quinoline's K_d for pH 4.2 and again at pH 7.5 for the situation where quinoline is present in very low concentrations, we use Eq. 11-117 and obtain

$$\begin{aligned} K_d(\text{pH} = 4.2) &= \frac{(0.0048)(20) + (20 \cdot 8.4 \times 10^{-2} / 2 \times 10^{-2})^{1/2} (10^{-4.2} / 10^{-4.94})}{1 + (10^{-4.2} / 10^{-4.94})} \\ &= \frac{0.096 + 48}{1 + 5.2} \\ &= 7.8 (\text{mol} \cdot \text{kg}^{-1}) \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \end{aligned} \quad (11-119)$$

and

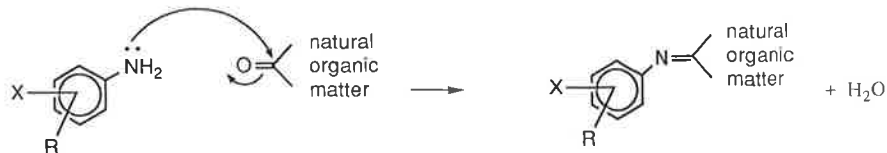
$$\begin{aligned} K_d(\text{pH} = 7.5) &= \frac{(0.0048)(20) + (20 \cdot 8.4 \times 10^{-2} / 2 \times 10^{-2})^{1/2} (10^{-7.5} / 10^{-4.94})}{1 + (10^{-7.5} / 10^{-4.94})} \\ &= \frac{0.096 + 0.025}{1 + 0.0028} \\ &= 0.12 (\text{mol} \cdot \text{kg}^{-1}) \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \end{aligned} \quad (11-120)$$

Zachara et al. (1986) measured $K_d(\text{pH} = 4.2) = 3.5$ and $K_d(\text{pH} = 7.5) = 0.75$, so it is obvious that our estimates of some inputs (e.g., σ_{ie} and K_{ie}) may not be accurate. Nonetheless we can get within a factor of a few, and even start to discern which sorption mechanisms are most important. For example, the K_d expressions show that at pH 4.2 most of the sorbed quinoline is accumulated through the ion exchange mechanism (i.e., the second term in the numerator is greatest), while at pH 7.5 similar amounts are sorbed to the natural organic matter and included as counterions in the film of water surrounding the particle surface.

Estimation of the Contribution of Surface Reactions

Organic Sorbate–Natural Organic Matter Reactions Until this point in the discussion, we have focused on cases where we could neglect chemical bond formation between the sorbate and materials in the solid phase. However, at least two kinds of *surface reactions* are known to be important for sorption of some chemicals (referred to as *chemisorption*). First, some organic sorbates can react with organic moieties contained within the natural organic matter of a particulate phase. Especially prominent in this regard are organic bases like substituted anilines (Hsu and Bartha, 1974, 1976). Due to their low pK_a 's (~ 5), the aromatic amine functionality is mostly not protonated at natural water pH's. When compounds like 3,3'-dichlorobenzidine are mixed with sediment, they become irretrievable using organic solvents that should

remove them from sorbed positions within natural organic matter or using salt solutions that should displace them from ion exchange sites (Appleton et al., 1980). Conditions that promote hydrolysis (see Chapter 12) do release much of these added aniline derivatives. Thus, it appears that reactions between the basic amine and carbonyl functionalities in the natural organic matter explain the strong sorption seen (Stevenson, 1976):



(11-121)

Such reactions often proceed slowly over hours, days, and even years, so the extent of this sorption due to organic chemical:organic chemical reactions is difficult to predict. Furthermore, such bond-forming sorption is sometimes irreversible on the timescales of interest, and we might not wish to include these effects in a K_d expression reflecting sorption equilibrium.

Organic Sorbate-Inorganic Solid Surface Reactions A second type of reaction exhibited by some organic chemicals involves bonding with atoms (e.g., metals) contained on the surface of the solid. Examples of such reactions are shown in Table 11.6. In these cases a hydroxyl bound to a metal in the solid is displaced by the organic sorbate. Given this additional sorption mechanism, the distribution coefficient becomes more complicated:

$$K_{d, \text{ion exchange and surface reaction}} = \frac{\left[\begin{array}{c} \text{organic counterion} \\ \text{near the surface} \end{array} \right] + \left[\begin{array}{c} \text{organic ion bound} \\ \text{to the surface} \end{array} \right]}{[\text{organic ion in solution}]} \quad (11-122)$$

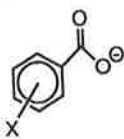
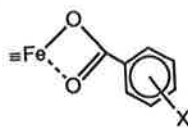
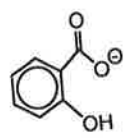
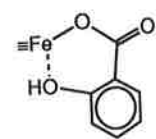
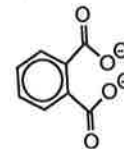
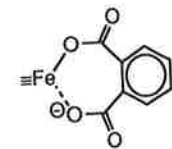
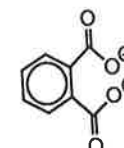
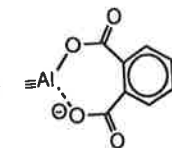
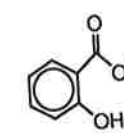
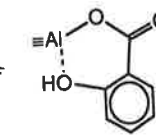
Here we assume that we can neglect neutral species, though this may not always be true. We can separate Eq. 11-122 into parts:

$$K_{d, \text{ion exchange and surface reaction}} = \frac{[\text{organic counterion}]}{[\text{organic ion in solution}]} + \frac{[\text{organic ion bound to surface}]}{[\text{organic ion in solution}]} \quad (11-123)$$

and use a previous result (e.g., Eq. 11-83) to write

$$K_{d, \text{ion exchange and surface reaction}} = \frac{\sigma_{ie} \cdot A \cdot K_{ie}}{[\text{competing ion}] + K_{ie} [\text{organic ion in solution}]} + \frac{[\text{organic ion bound to surface}]}{[\text{organic ion in solution}]} \quad (11-124)$$

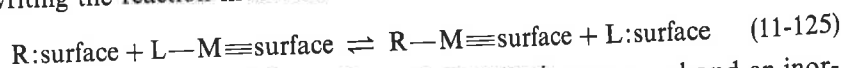
TABLE 11.6 Examples of Organic Sorbates Reacting with Mineral Surfaces^a

TABLE 11.6 Examples of Organic Sorbates Reacting with Mineral Surfaces						Ref. ^b
$\equiv\text{Fe}-\text{OH}$	+		\rightleftharpoons		+ OH^-	1
Substituted Benzoates						
$\equiv\text{Fe}-\text{OH}$	+		\rightleftharpoons		+ OH^-	2,3
Salicylate						
$\equiv\text{Fe}-\text{OH}$	+		\rightleftharpoons		+ OH^-	2,4
o-Phthalate						
$\equiv\text{Al}-\text{OH}$	+		\rightleftharpoons		+ OH^-	5
o-Phthalate						
$\equiv\text{Al}-\text{OH}$	+		\rightleftharpoons		+ OH^-	5
Salicylate						

^aOnly limited information is available regarding the bonding of species to water-wet surfaces; thus the bonding of the sorbates shown here is conjecture.

^b1. Kung and McBride, 1989. 2. Balistrieri and Murray, 1987. 3. Yost et al., 1990. 4. Lövgren, 1991. 5. Stumm et al., 1980.

Now our task is to develop an expression to predict the last term. To do this, we begin by writing the reaction involved:



where $\text{R}-\text{M}\equiv\text{surface}$ and $\text{L}-\text{M}\equiv\text{surface}$ are an organic compound and an inorganic ligand like $-\text{OH}$ bonded to the solid as indicated by the hyphen. The ions

R:surface and L:surface are present at the concentrations in the immediate vicinity of the reaction site, that is, in the diffuse double layer (Region II in Fig. 11.18). Such a reaction reflects a free energy change that we will refer to as ΔG_{rxn} and a corresponding equilibrium expression:

$$K_{\text{rxn}} = \frac{[\text{R}-\text{M}\equiv\text{surface}][\text{L:surface}]}{[\text{R:surface}][\text{L}-\text{M}\equiv\text{surface}]} \quad (11-126)$$

If we can assume that there are a finite number of reactive sites on the solid, σ_{rxn} ($\text{mol}\cdot\text{m}^{-2}$), then we have

$$A\cdot\sigma_{\text{rxn}} = [\text{R}-\text{M}\equiv\text{surface}] + [\text{L}-\text{M}\equiv\text{surface}] \quad (11-127)$$

with A equal to the specific particle surface area (meter squares per kilogram). Therefore, we can rewrite Eq. 11-126:

$$K_{\text{rxn}} = \frac{[\text{R}-\text{M}\equiv\text{surface}][\text{L:surface}]}{[\text{R:surface}](A\cdot\sigma_{\text{rxn}} - [\text{R}-\text{M}\equiv\text{surface}])} \quad (11-128)$$

We also recall from Eqs. 11-86 and 11-87 that the concentrations of ions in the layer of water next to the particle surface can be related to the corresponding species in the bulk solution:

$$[\text{L:surface}] = [\text{L}^-]_{\text{bulk}} \cdot e^{-\Delta G_{\text{elect}}/RT} \quad (11-129)$$

and

$$[\text{R:surface}] = [\text{R}^-]_{\text{bulk}} \cdot e^{-\Delta G_{\text{elect}}/RT} \cdot e^{-\Delta G_{\text{hydrophob}}/RT} \quad (11-130)$$

Using these relations in Eq. 11-128, along with Eq. 11-88, we have

$$\begin{aligned} K_{\text{rxn}} &= \frac{[\text{R}-\text{M}\equiv\text{surface}][\text{L}^-]_{\text{bulk}} e^{-\Delta G_{\text{elect}}/RT}}{(A\cdot\sigma_{\text{rxn}} - [\text{R}-\text{M}\equiv\text{surface}])[\text{R}^-]_{\text{bulk}} e^{-\Delta G_{\text{elect}}/RT} e^{-\Delta G_{\text{hydrophob}}/RT}} \\ &= \frac{[\text{R}-\text{M}\equiv\text{surface}][\text{L}^-]_{\text{bulk}}}{(A\cdot\sigma_{\text{rxn}} - [\text{R}-\text{M}\equiv\text{surface}])[\text{R}^-]_{\text{bulk}} K_{\text{ie}}} \end{aligned} \quad (11-131)$$

Simplifying and rearranging, we then find:

$$[\text{R}-\text{M}\equiv\text{surface}] = \frac{\sigma_{\text{rxn}} \cdot A \cdot K_{\text{ie}} \cdot K_{\text{rxn}} \cdot [\text{R}^-]_{\text{bulk}}}{[\text{L}^-]_{\text{bulk}} + K_{\text{ie}} \cdot K_{\text{rxn}} \cdot [\text{R}^-]_{\text{bulk}}}$$

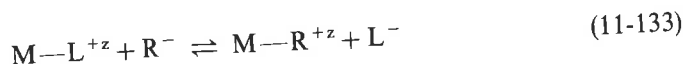
Thus another Langmuir isotherm is expected with the maximum bound concentrations equal to $\sigma_{\text{rxn}} \cdot A$ and the K_{Langmuir} given by $K_{\text{rxn}} \cdot K_{\text{ie}} \cdot [\text{L}^-]_{\text{bulk}}^{-1}$. This result is very

similar in form to that seen before for an ion exchange process (Eq. 11-83). Returning to our overall K_d expression (Eq. 11-124), we can now write

$$K_{d, \text{ion exchange and surface reaction}} = \frac{\sigma_{ie} \cdot A \cdot K_{ie}}{[\text{competing ion}] + K_{ie}[\text{organic ion}]} + \frac{\sigma_{rxn} \cdot A \cdot K_{ie} \cdot K_{rxn}}{[\text{competing ligand}] + K_{ie} \cdot K_{rxn} \cdot [\text{organic ion}]} \quad (11-132)$$

As for nonreacting organic ions, we need information on the ion exchange tendency of the chemical of interest (K_{ie} or $\Delta G_{\text{hydrophob}}$); now we also need a means to assess K_{rxn} .

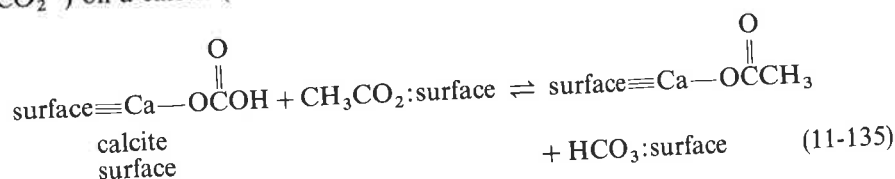
We can evaluate K_{rxn} recognizing that the tendency to form chemical linkages to solid surface atoms correlates with the likelihood of forming comparable complexes in solution (Stumm et al., 1980; Schindler and Stumm, 1987; Dzombak and Morel, 1990). That is, the free energy change associated with the exchange shown by Eq. 11-125 appears energetically similar to that for a process occurring between two dissolved components:



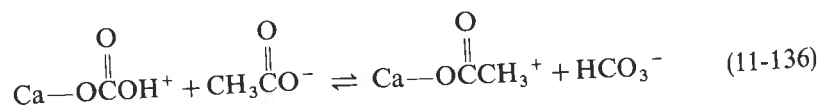
where $z + 1$ would be the charge of the free metal in aqueous solution. This entirely solution-phase exchange reaction is characterized by an equilibrium constant:

$$K_{\text{ligand exchange in solution}} = \frac{[M-R^{+z}][L^{-}]}{[M-L^{+z}][R^{-}]} \quad (11-134)$$

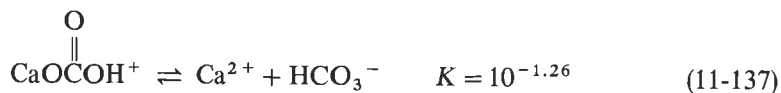
A substantial data base is available to quantify such solution equilibria (e.g., Martell and Smith, 1977; Morel, 1983). Let us examine a specific case. For example, we might be interested in the replacement of a bicarbonate ligand (HCO_3^{-}) by acetate ($\text{CH}_3\text{CO}_2^{-}$) on a calcite (CaCO_3) surface:



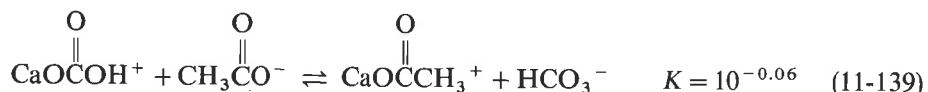
This surface reaction of acetate enables an adsorbed species to be formed which is different from acetate ions simply contained within the electric double layer. To assess this surface reaction, we examine the comparable solution case:



For the case of acetate exchange with bicarbonate in aqueous solution, we can find for aqueous solution (Morel, 1983):



and combining:



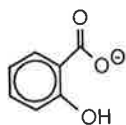
This result for the overall solution equilibrium implies that the free energy change of this particular ligand exchange in solution is near zero ($\Delta G_{\text{rxn}} = -RT \ln 10^{-0.06} = 0.3 \text{ kJ} \cdot \text{mol}^{-1}$). This may not be too surprising in light of the chemical similarity of bicarbonate and carboxylate anions. Further, it seems very likely that other longer-chain carboxylic acids (i.e., fatty acids) will also exhibit the similar solution-phase reactivity with calcite.

Now we make use of the very important idea that such solution-phase equilibria can be used to estimate ΔG_{rxn} for comparable surface ligand exchanges. For the specific case of acetate binding to calcite, we would estimate

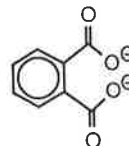
$$\Delta G_{\text{rxn}} \approx \Delta G_{\text{ligand exchange in solution}} = 0.3 \text{ kJ} \cdot \text{mol}^{-1} \quad (11-140)$$

Therefore, we estimate that K_{rxn} is 0.9 and use it in Eq. 11-132 for calculating K_d for the sorption of acetate on calcite.

The procedure for other charged organic chemicals is analogous; and by using the results in Eq. 11-132, we begin to build an overall estimate of charged organic chemical sorption to minerals. Generally, it seems that the tendencies of monodentate organic ligands (e.g., RCOO^- , ϕOH , RNH_2) to displace inorganic ligands at mineral surfaces is not very great, and it may be reasonable to neglect such surface-bound species when considering the overall K_d of such simple organic sorbates. However,



Salicylate

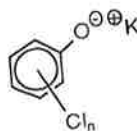


o-Phthalate

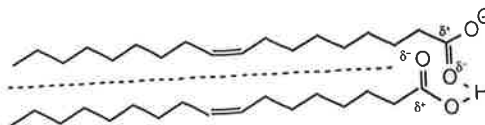
since even a small degree of adsorption can be important to the rate of heterogeneous transformations (e.g., Ulrich and Stone, 1989), in some cases we may need to deal with this. Other charged organic sorbates like salicylate or *o*-phthalate, which may form two bonds with the mineral, are much more likely to exhibit significant ΔG_{rxn} contributions to the overall ΔG_{ads} (Schindler and Stumm, 1987).

Summary Comments Regarding Sorption of Charged Organic Compounds

Before we conclude, we should note that the simple K_d formulations used here may not reflect all the possible mechanisms of charged organic chemical sorption. Frequently we assume sufficient f_{om} to neglect associations of the neutral organic species with mineral surfaces. Similarly, we presumed that charged organic molecules would not "dissolve" into natural organic matter, and Schellenberg et al. (1984) observed sorption of trichlorophenolates consistent with this picture. However, these workers also found that pentachlorophenolate exhibited K_d 's far in excess of expectations. Further studies (Westall et al., 1985) indicated that this may be due to the sorptive uptake of the potassium phenolate complex or ion pair



into the natural organic matter. If true, this would require the inclusion of more species in the initial K_d formulation and also thermodynamic expressions relating these species to the phenolate dissolved. In another case, Jung et al. (1987) interpreted oleic acid adsorption to iron oxides as including some role of a neutral oleic acid:oleate complex:



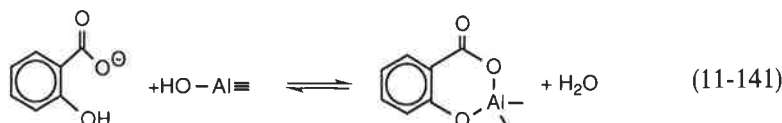
This is reminiscent of the hemimicelle cases we discussed, where now substantial aggregation in solution occurs for only pairs of molecules. Under solution conditions where these "new" species arise, obviously we must (1) adjust the starting K_d expressions to include them, and (2) utilize equilibrium information relating them to the nonassociated species.

11.7 SORPTION KINETICS

Thus far we have focused on situations in which the time was sufficient to allow solid-water exchange of chemicals to achieve equilibrium. However, sometimes we are concerned with cases where the solids do not remain in contact with the solutions

of interest for long. Examples of such short-contact situations include storm-related sediment resuspensions or soil erosion events where, after calm is restored, the particles quickly settle to the sediment bed. In another case, zooplankton fecal pellets of approximately 100 μm diameter fall through a body of water at about 100 m/day, conceivably too fast to permit sorbates to establish sorption equilibrium with each depth interval of the surrounding water. Infiltrating groundwater may experience only brief contact with the soil grains by which these solutions pass. Even groundwater moving at natural slow flow rates may not always expose the aquifer solids long enough to permit complete sorption equilibrium (Roberts et al., 1986; Ball and Roberts, 1991). In all of these cases, certain molecules may simply not have enough time to exchange before the solution or the solid moves away from the other phase. Sometimes slow desorption also limits transformations like biodegradation (Rijnaarts et al., 1990).

Two types of processes could act as the bottleneck, inhibiting sorptive equilibrium. First, chemical reactions (*chemisorption*) between the sorbate and the point of association in the particles might limit the overall approach to sorptive equilibrium. An example is salicylate sorption to very small alumina particles (Kummert and Stumm, 1980). Most of the sorbed salicylate is thought to be chemically bound to the alumina surface:



During the short interval (< 2 h) after initial mixing of the salicylate with the alumina, dissolved salicylate concentration drops quickly and then decreases more gradually (Fig. 11.28a). Apparently, the rate of salicylate reaction with surface sites on the exterior of the particles is controlling the rate of overall sorption during the early portion of this timecourse. Another example of chemisorption might be slow condensation reactions of organic amines with carbonyl moieties of the solid phase natural organic matter. To quantify the kinetics of these particular chemisorption processes, one needs to deal with the rates of the individual reactions involved.

The second type of limitation occurs when the sorbate molecules do not physically have enough time to move to all the points of contact in and on the solids where they would become associated. We often refer to this physical limitation as a *mass transfer limited process*. For example, we can imagine charged sorbate molecules needing time to diffuse into a clayey floc before they can associate with oppositely charged surface sites in the interior (Fig. 11.28b). Similarly, we can easily see that some of the natural organic matter that absorbs nonpolar compounds may be located at somewhat inaccessible positions within silty aggregates (Fig. 11.28c). Even in the case of ligand exchange, as for salicylate ions, diffusion into porous alumina particles where there are more reactive sites can be slow (Fig. 11.28a for times greater than a few hours). Since sorptive equilibrium is only reached when each subpart of a solid has accumulated enough sorbate to itself be equilibrated with the solution on the outside, we can

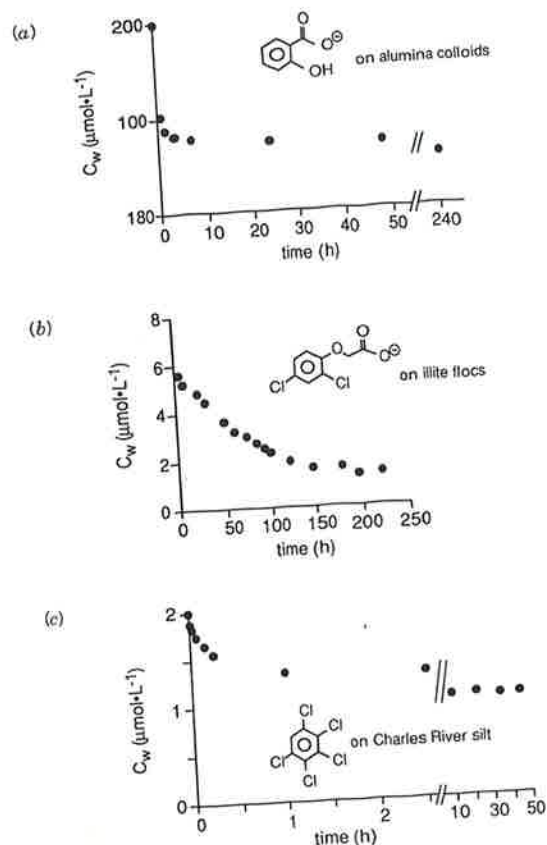


Figure 11.28 Some observed time courses of organic compounds associating with suspended solids. (a) Salicylate sorption to 20 nm $\gamma\text{-Al}_2\text{O}_3$ (data from Kummert and Stumm, 1980). (b) 2,4-D sorption to clay flocs (data from Haque et al., 1968). (c) Pentachlorobenzene sorption to silt-sized river sediment (data from Wu and Gschwend, 1986).

recognize that simply delivering molecules to all the internal solid "binding" sites must take a finite amount of time. Once the molecules have arrived at the particulate locations where they will be bound, then interactions may occur on the molecular scale. If the average time spent arriving at these local points of association is long compared to the time required to make these molecule-scale attachments, then we must focus on the rate of molecular penetration to the binding sites to describe the overall sorption kinetics. Many reports suggest that the molecule-scale sorbate-sorbent association is fast relative to diffusion within porous solids (e.g., Helfferich, 1962, or Adamson, 1982, regarding ion exchange; e.g., Brusseau and Rao, 1989 review of nonpolar organic chemical sorption). Therefore, in the following discussions, we focus on cases of mass transfer limitations to solid-water exchange and the resultant approach one may use to estimate overall sorption rates.

Sorption Kinetics for Mass Transfer Limited Mechanisms

We begin by noting that soil and sediment particles are often actually present as *aggregates* of individual solid phases (Fig. 11.29). Not only does this refer to the coalescence of many fine grains such as those seen in flocculated clay aggregates, but may also include parent mineral grains coated with other phases like iron oxides and natural organic matter. The resultant solids are then composed of subregions with differential capabilities to sorb organic compounds. A key exception to this extremely porous visualization involves sands or larger rocks which consist of individual grains (e.g., quartz). Even such "single solid" natural particles contain some micropores (e.g., Wood et al., 1990; Ball et al., 1990), and passing through these pores sometimes appears to be critical for accessing the quantitatively most important sorption sites.

For molecules in solution to distribute themselves between the dissolved and sorbed phases, several steps in series are required. First, there may be a mass transfer limitation due to diffusion across a poorly mixed water layer surrounding the outside of each particle (Fig. 11.29). The timescales of such external diffusion are probably on the order of seconds in most turbulent situations. Using Eq. 9-31, we can get an estimate of this timescale:

$$\tau \sim \frac{(\text{thickness of boundary layer surrounding aggregate})^2}{2D_w} \quad (11-142)$$

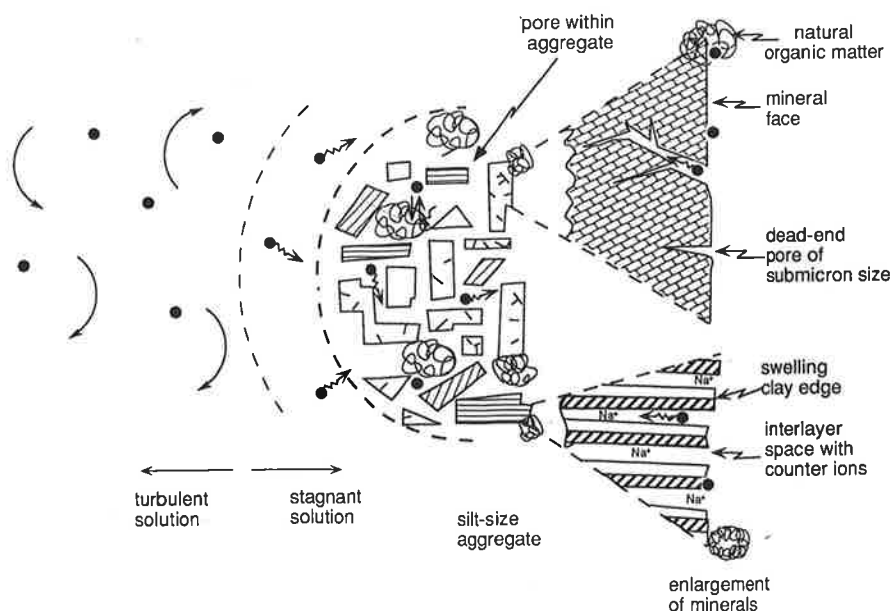


Figure 11.29 Conceptualization of the sequence of steps required to move sorbate molecules (pictured as black dots) between a turbulent solution and all the sorptive sites within a typical soil or sediment aggregate.

For relatively large particles ($> 200 \mu\text{m}$), like sands whose surfaces are large enough to impart significant frictional interaction with the fluids, such a boundary layer thickness is probably on the order of $200 \mu\text{m}$ in thickness. For smaller particles ($\lesssim 200 \mu\text{m}$), the diffusion limited zone shrinks in proportion to the particle size. Thus $200 \mu\text{m}$ might typify the largest boundary thickness we encounter. Together with a reasonable value of D_w (see Fig. 9.7), we find that external diffusion requires on the order of

$$\tau \sim \frac{(2 \times 10^{-2} \text{ cm})^2}{2(10^{-5} \text{ cm}^2/\text{s})} \quad (11-143)$$

$\sim 20 \text{ s}$

Obviously, if the solution outside the particles is mixed at all, there will not be much time spent by molecules reaching the aggregate exterior. In nonturbulent solutions like groundwater or sediment porewaters, the distance between grain surfaces is probably about the same as the grain size. Consequently, use of an equation analogous to Eq. 11-142 would show a timescales of diffusion in the intergranular solutions of only seconds to minutes at most. If the primary site of attachment is on the exterior surface of the particles, then the overall sorption process will be characterized by this external diffusion time plus that required to complete the local binding reaction. This is probably the appropriate image of what is controlling sorption of salicylate to alumina at early times, as we discussed above (Fig. 11.28a).

For many natural particles of interest (e.g., soils, suspended solids), the sorbates must continue their transport to their ultimate points of attachment by diffusing in the *immobile* fluids filling the interstices of the aggregates (Fig. 11.29; Rao et al., 1980, 1982; Wu and Gschwend, 1986, 1988; Weber et al., 1991). Generally, such pore spaces are large relative to the molecules themselves (i.e., these pores are probably about the same size as the parent particles of which the aggregate is made); thus diffusion in these spaces occurs somewhat like molecular diffusion in aqueous solution. An exception may be that some pore spaces are blocked by natural organic matter, and molecular transfer to points deeper in the aggregate interior or even deep inside the natural organic matter may require diffusion through these organic polymers (Brusseau and Rao, 1989; Brusseau et al., 1991; Brusseau and Rao, 1991). If the majority of solid sorbent is accessed after diffusion through "large pores", then the overall process may be effectively described by focusing on this step.

Other times, the bulk of the sorption occurs at quite inaccessible positions such as in *dead-end pores* or between the layers of aluminosilicate minerals (Ball and Roberts, 1991). These channels differ from those of the aggregate in that they exhibit openings that are comparable in size to the sorbate molecules of interest. This results in a *steric limitation* to diffusive transport. Also, these channels are probably not as extensively interconnected (hence the "dead-end" reference) as those between the grains making up aggregates. This also contributes to inhibiting exchange with the exterior. When the sorption sites of interest involve these kinds of solid positions, then we may consider the mass transfer to involve diffusion coefficients that are greatly

reduced relative to the free solution values. Various reports of extremely slow desorption kinetics (decade timescales) such as those seen for residues of the soil fumigant, ethylene dibromide, appear to be best explained by release from such poorly accessible nanometer-sized pores (Steinberg et al., 1987).

Modeling Mass Transfer Limited Sorption

Since sorption kinetics experiments usually reveal an early period of extensive exchange, followed by a prolonged time of slowly proceeding uptake (or release) by particles (Leenheer and Ahlrichs, 1971; Connolly, 1980; Karickhoff, 1980; Wu and Gschwend, 1986; Brusseau and Rao, 1989; Ball and Roberts, 1991), the sorption process has been characterized with a two-box model (Karickhoff, 1980). In this conceptualization, one portion of the solid phase is taken to be rapidly equilibrated with the solution phase; the other part of the solid is described using a rate equation. One can easily extend this idea by imagining an infinite series of "boxes" in the particles, each in successively less direct contact with the exterior solution. That is the approach used here. Thus our problem entails diffusing sorbate molecules *radially* via the interconnecting porewater channels into soil or sediment aggregates. Such a picture may be well suited to cases in which most of the organic sorbate of concern will eventually be associated with relatively accessible solid phases like natural organic matter. Although real-world particles are not spherical, and the points of sorptive attachment may not be spread evenly throughout the natural particle aggregate, these characteristics are reasonable approximations.

To describe this transfer of sorbate molecules into or out of such aggregates, we first consider a single porous sphere of radius R (Fig. 11.30). The solute concentration

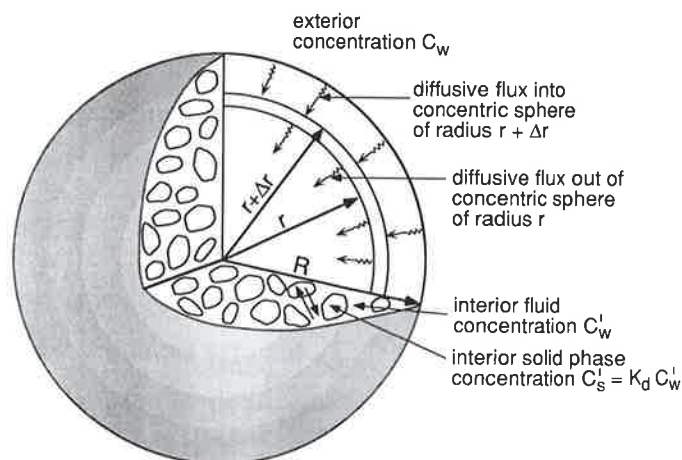


Figure 11.30 Diffusion-limited transfer into an idealized soil or sediment aggregate of radius R and interior concentrations $C'_w(r,t)$ in the water within the aggregate. Sorption is modeled using a mass balance equation for any concentric shell of thickness Δr (see Eq. 11-153 in text).

inside the aggregate pores, C'_w , is always at equilibrium with the adjacent sorbed phase, C'_s :

$$C'_s = K_d^* C'_w \quad (11-144)$$

where K_d^* is the *in situ* (microscopic) distribution coefficient. Ultimately, we are interested in the "macroscopic" distribution coefficient that relates the (macroscopic) sorbed concentration, C_s , to the dissolved concentration in the exterior water, C_w :

$$C_s(t) = K_d(t) \cdot C_w \quad (11-145)$$

where, owing to finite kinetics of macroscopic sorption, K_d is time dependent.

Note that C_s is determined as the total mass of the compound in the dried particle divided by the dry particle mass. Thus, C_s includes the dissolved fraction of the chemical in the porewater when the particles are dried. Due to the spherical symmetry, the evolving concentration distributions only depend on the radial distance r and on time t . The total concentration in the particle at distance r from the center, C_{tot} , on a particle volume basis is given by

$$C_{tot}(r) = \rho_s(1 - \phi)C'_s(r) + \phi C'_w(r) \quad (\text{mol} \cdot \text{L}^{-1}) \quad (11-146)$$

where ρ_s is the density of (dry) solid ($\text{kg} \cdot \text{L}^{-1}$ solid) and ϕ is the porosity of particle aggregate ($\text{L water} \cdot \text{L}^{-1}$ total).

Since C'_s and C'_w are related by Eq. 11-144, we get

$$C_{tot}(r) = [K_d^* \cdot (1 - \phi) \cdot \rho_s + \phi] \cdot C'_w(r) \quad (11-147)$$

When K_d^* , ρ_s , and ϕ are constant everywhere within the particle aggregate, the mean total concentration in the particle is

$$\bar{C}_{tot} = [K_d^* \cdot (1 - \phi) \cdot \rho_s + \phi] \cdot \bar{C}'_w \quad (11-148)$$

where

$$\begin{aligned} \bar{C}'_w &= \frac{\int_0^R 4\pi r^2 \cdot C'_w(r) dr}{4\pi R^3/3} \\ &= \frac{3}{R^3} \int_0^R r^2 C'_w(r) dr \end{aligned} \quad (11-149)$$

is the volume-weighted mean of the radial concentration field $C'_w(r)$. The (macroscopic)

sorbed concentration on a particle mass basis now can be calculated:

$$C_s = \frac{\bar{C}_{\text{tot}}}{\rho_{\text{bulk}}} = \frac{\bar{C}_{\text{tot}}}{(1-\phi)\rho_s} = \left[K_d^* + \frac{\phi}{(1-\phi)\rho_s} \right] \bar{C}_w \quad (11-150)$$

where C_s is a function of time like \bar{C}_w .

To make the last step to Eq. 11-145, we have to relate the time-dependent mean concentration \bar{C}_w to the external solute concentration C_w . If the sorbate molecules only diffuse in the pores, we recognize that the change in total sorbate concentration \bar{C}_{tot} is controlled by diffusive uptake through the pore fluids driven by gradients in the internal sorbate concentration C'_w . Thus, we consider our single porous sphere of radius R to have sorbate molecules diffusing through successive concentric layers (Fig. 11.30). Diffusion into or out of the sphere begins at $t = 0$, and it occurs because of a difference in concentrations between the inside porewater and the outside bulk solution. If we consider a mass balance equation for any thin concentric shell within the spherical aggregate, bounded by spheres with radius r and $r + \Delta r$, we may write

$$\frac{\partial C_{\text{tot}}}{\partial t} = \frac{\text{Flux at inner sphere} - \text{Flux at outer sphere}}{\text{shell volume}} \quad (11-151)$$

Using Eq. 9-2, multiplied by the areas of the relevant shells, to quantify the fluxes in Eq. 11-151, and assuming that dissolved concentration changes along the radial directions are responsible for diffusive transport, we have

$$\begin{aligned} \frac{\partial C_{\text{tot}}}{\partial t} &= \frac{-\left(\phi \cdot D \cdot 4\pi r^2 \cdot \frac{\partial}{\partial r}(C'_w)\right) + (\phi \cdot D \cdot 4\pi(r + \Delta r)^2) \cdot \frac{\partial}{\partial r}\left(C'_w + \Delta r \frac{\partial C'_w}{\partial r}\right)}{(4/3)\pi(r + \Delta r)^3 - (4/3)\pi r^3} \\ &= \frac{-4\pi D \phi(r)^2 \cdot \left(\frac{\partial C'_w}{\partial r}\right) + 4\pi D \phi(r + \Delta r)^2 \left(\frac{\partial C'_w}{\partial r} + \Delta r \frac{\partial^2 C'_w}{\partial r^2}\right)}{(4/3)\pi(r + \Delta r)^3 - (4/3)\pi r^3} \end{aligned} \quad (11-152)$$

where we have estimated the concentration gradient at the radius $r + \Delta r$ to be approximated by the linear expansion, $C'_w(r + \Delta r) \simeq C'_w(r) + \Delta r \frac{\partial C'_w}{\partial r}$. We have also reduced the fluxes in proportion to the aggregate porosity ϕ to account for the diminished cross-sectional area available for diffusion. Neglecting all terms of order $(\Delta r)^2$ or $(\Delta r)^3$, we can simplify to find

$$\frac{\partial C_{\text{tot}}}{\partial t} = \phi D \left(\frac{\partial^2 C'_w}{\partial r^2} + \frac{2}{r} \frac{\partial C'_w}{\partial r} \right) \quad (11-153)$$

To use this equation we need to consider what factors dictate the magnitude of D . First, of course, we know from our physical conceptualization that we are interested in molecules diffusing in aqueous solutions in the aggregate pores; hence D should be closely related to D_w , the molecular diffusivity in water. Unlike diffusion in water though, the sorbate molecules must navigate around the various fine grains making up the skeleton of our natural particle aggregate. This elongated path issue is treated by using a tortuosity factor f which reduces D to some value below D_w . If the size of the pores is small enough to be comparable to the diffusing molecules themselves, we also need to reduce D_w again using what is called a constrictivity factor (Satterfield et al., 1973; Ball and Roberts, 1991). It is also possible that diffusion occurs, not only in the water filling the pores, but also on the walls of the component particles in a two-dimensional process called surface diffusion. Here we neglect this process because of the discontinuous nature of the aggregates.

Returning to Eq. 11-153, C_{tot} can be replaced by C'_w using Eq. 11-147. Note again that ϕ , K_d^* , and ρ_s are assumed to be spatially constant. Thus,

$$\frac{\partial C'_w}{\partial t} = D^* \left[\frac{\partial^2 C'_w}{\partial r^2} + \frac{2}{r} \frac{\partial C'_w}{\partial r} \right] \quad (11-154)$$

with

$$D^* = \frac{\phi f D_w}{K_d^*(1 - \phi)\rho_s + \phi} \quad (11-155)$$

D^* is sometimes referred to as the effective diffusivity.

The time-dependent solution for C'_w which satisfies Eq. 11-154 is an infinite sum of exponential terms (Crank, 1975). If we consider the relative approach to equilibrium using the total mass of sorbate inside the solid phase at time t , $\bar{C}_{tot}(t)$, versus the final mass accumulated at steady-state, $\bar{C}_{tot,\infty}$, then the ratio of these sorbed phase loadings, $\bar{C}_{tot}(t)/\bar{C}_{tot,\infty}$, depends on a nondimensional parameter, $D^* \cdot t/R^2$:

$$\frac{\bar{C}_{tot}(t)}{\bar{C}_{tot,\infty}} = F\left(\frac{D^* t}{R^2}\right) \quad (11-156)$$

where F is a monotonically increasing function with $F(0) = 0$ and $F(1) = 1$. The larger is the sorbate's effective diffusivity, the faster will be the approach to equilibrium. Conversely, the larger the particle, the slower will be the overall sorptive equilibrium since diffusion pathlengths are longer.

We can picture the corresponding concentration profiles (Fig. 11.31) for the case where the exterior solution exhibits a constant concentration C_w and the molecules are diffusing into a spherical aggregate of interest. Upon initial mixing, the outermost portion of the sphere equilibrates with the solution so that this part of the sorbent exhibits sorbed concentration $K_d \cdot C_w$. Subsequently, more interior portions of the sphere accumulate the sorbate, and it is these integrated concentrations, weighted for

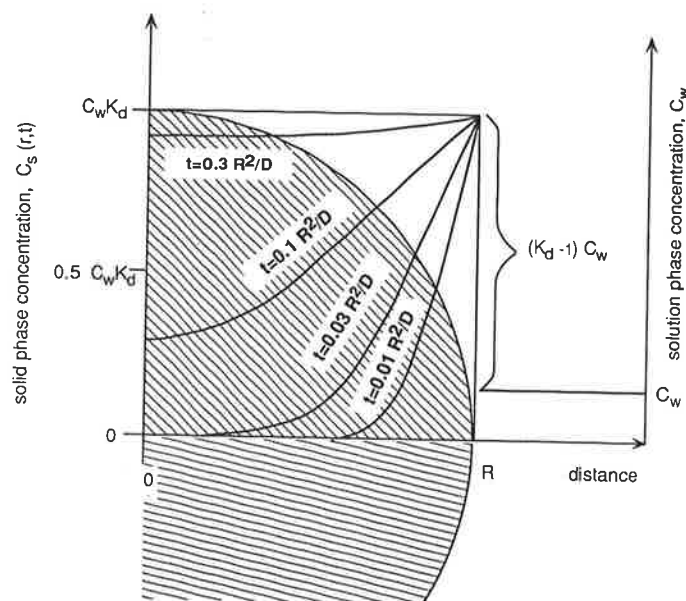


Figure 11.31 Concentration profiles resulting from the diffusion of a sorbate into a porous particle from a solution of constant concentration C_w . Successive profiles are characterized by times given as a function of R , the particle radius, and D^* , the effective diffusivity of the sorbate moving into the particle.

the concentric volumes they occupy, that correspond to the time-varying sorbed load. When $t \approx 0.03 R^2/D^*$, the total sorbed load is about 50% of its equilibrium value, and when $t \approx 0.3 R^2/D^*$, the process is 97% complete. Put another way, the solid phase is virtually "filled up" with sorbate (Fig. 11.31), and we might define an approximate sorption rate constant for this case of constant exterior solution concentration:

$$k_{\text{sorb}}(C_w = \text{constant}) \approx \frac{\ln 2}{t_{50\%}} \approx \frac{0.69 D^*}{0.03 R^2} \approx 23 D^*/R^2 \quad [\text{T}^{-1}] \quad (11-157)$$

Use of such an approximate first-order rate constant yields a result similar to that obtained from the complete solution (Crank, 1975), but it underpredicts sorptive exchange at short times and overpredicts sorption at long times (Fig. 11.32).

In the cases where C_w does not remain constant in the exterior solution (because a significant portion of the dissolved load is sorbed), the expression for k_{sorb} becomes a little more complicated (Crank, 1975; Wu and Gschwend, 1988). Figure 11.33 shows how the progress of sorptive exchange proceeds for several different values of $K_d \cdot r_{\text{sw}}$ (which characterizes the proportion of the total chemical in the system eventually sorbed). As $K_d \cdot r_{\text{sw}}$ increases from the infinite bath case (i.e., $C_w = \text{constant}$), we see that the times required to reach equilibrium decrease. For cases of sorptive uptake,

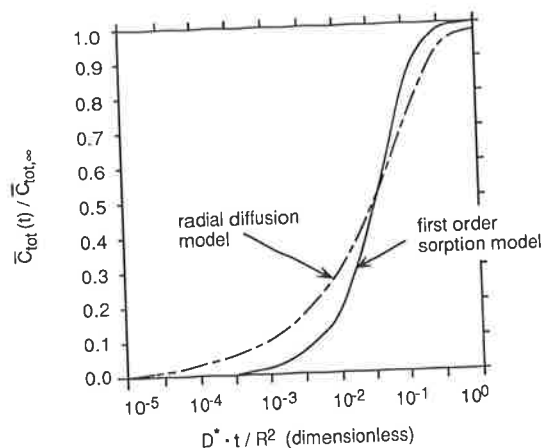


Figure 11.32 Comparison of the exact solution to the radial diffusion model of sorptive exchange from Crank (1975) with the first-order model approximation. $\bar{C}_{tot}/\bar{C}_{tot,\infty}$ is the ratio of the current average solid-phase sorbate concentration to that achieved at equilibrium; D^* is the effective diffusivity of a sorbate moving within the sorbent; R is the sorbent radius; and t is time.

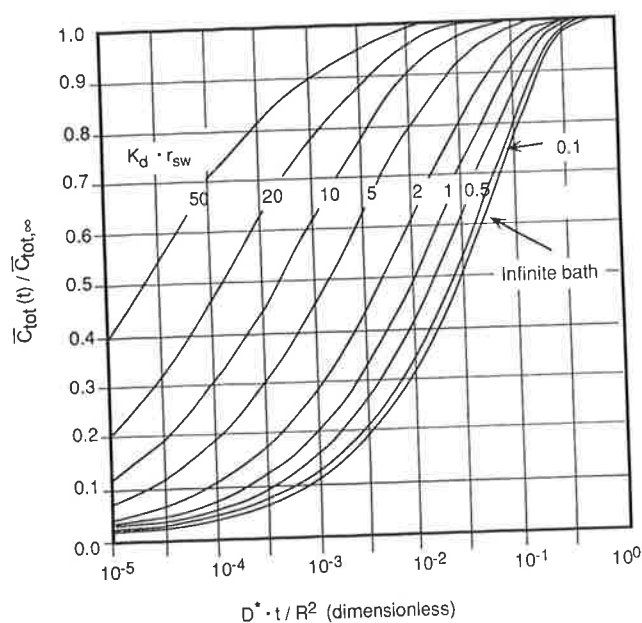


Figure 11.33 Timecourses for the diffusive uptake or release of sorbates by spherical particles suspended in closed systems. The numbers on the curves show the final ratio of the mass sorbed on solids to the mass dissolved in the solution.

this might be understood by recognizing that the gradients $\partial C_w / \partial r$ will be steeper for longer if there are more solids or greater tendencies to sorb. For cases of desorption, this shortened time may be explained by realizing that each of the aggregates need only release a little sorbate to build up equilibrium levels in the solution.

Examining the curves for nonconstant C_w allows us to specify k_{sorb} when C_w is not a constant. For example, we may be interested in a case where $r_{\text{sw}} \cdot K_d$ is 10. To reach 50% sorption completion, we can use Figure 11.33 to see that the time required will be

$$t_{50\%}(K_d \cdot r_{\text{sw}} = 10) \simeq 4 \times 10^{-4} R^2 / D^* \quad (11-158)$$

or that the approximate first-order rate constant should be

$$k_{\text{sorb}}(K_d \cdot r_{\text{sw}} = 10) \simeq \frac{D^* \ln 2}{4 \times 10^{-4} R^2} \simeq 2000 D^* / R^2 \quad (11-159)$$

In general, the relation of k_{sorb} to $K_d \cdot r_{\text{sw}}$, optimized to fit the midpoint of the sorptive exchange, is given (Wu and Gschwend, 1988) by

$$k_{\text{sorb}}(K_d \cdot r_{\text{sw}}) \simeq (11 \cdot K_d \cdot r_{\text{sw}} + 23) D^* / R^2 \quad (11-160)$$

We should reiterate that this approximate solution is well suited for describing the midregion of the solid-water exchange timecourse, but does poorly for early and late times. Use of Figure 11.33 can allow one to be more accurate at $t_{10\%}$, $t_{90\%}$, or whatever extent of approach to sorptive equilibrium is of interest.

If one believes that a retarded radial diffusion mass transfer is limiting overall sorption, as did the authors who produced the data shown in Figure 11.28b and c, we now can see how such data can be used to deduce the critical ratio R^2 / D^* for situations of interest. For example, the uptake of 2,4-D by illite flocs, illustrated in Figure 11.28b, exhibits a $t_{50\%}$ of about 50 h. Since these particular data were obtained in experiments with $K_d \cdot r_{\text{sw}}$ of about 4, we may estimate

$$k_{\text{sorb}} \simeq \frac{\ln 2}{t_{50\%}} \simeq \frac{\ln 2}{50 \text{ h}} \sim 0.014 \text{ h}^{-1} \quad (11-161)$$

If we know the radius of the illite flocs, this result would allow us to estimate the effective diffusivity of 2,4-D in those aggregates.

These results also enable us to understand how K_d will vary with time. First, since \bar{C}'_w is proportional to \bar{C}_{tot} and increases until it equals C_w , we can write

$$\bar{C}'_w = (\bar{C}_{\text{tot}} / \bar{C}_{\text{tot}, \infty}) C_w \quad (11-162)$$

Inserting Eq. 11-162 into Eq. 11-150, we find

$$K_d(t) = \left(K_d^* + \frac{\phi}{(1-\phi)\rho_s} \right) (\bar{C}_{tot}/\bar{C}_{tot,\infty}) \quad (11-163)$$

$$= K_d^\infty \cdot (\bar{C}_{tot}/\bar{C}_{tot,\infty}) \quad (11-164)$$

with $K_d^\infty = K_d^* + \phi/(1-\phi)\rho_s$. Note that the second term on the right-hand side of our K_d^∞ expression simply reflects the uptake due to pore water reaching concentrations like that of the exterior solution. As for the variation of \bar{C}_{tot} , the value of K_d approximately represents an equilibrium condition at (e.g., five half-lives)

$$t \approx \frac{0.3 \cdot R^2}{D^*} = 0.3 \cdot R^2 \cdot \frac{K_d^*(1-\phi)\rho_s + \phi}{\phi f D_w} \quad (11-165)$$

An Example: Calculation of the Desorption Kinetics of an Organic Chemical Let us conclude this discussion with an example calculation to see how we might evaluate sorption kinetics in a particular case. For example, suppose we are concerned that some PCB-contaminated sediments will spill and settle through a water body during dredging operations. First, we note that the volume of water involved is probably very large compared to the mass of solids that we will spill; hence $K_d \cdot r_{sw}$ is a small number. In this event, we focus our attention on the timecourse in Figure 11.33 labeled "infinite bath" where $K_d \cdot r_{sw}$ is less than 0.01. Now if we are interested in finding the time necessary to desorb half of the PCB contaminants from the settling sediment grains, we read across the chart from $\bar{C}_{tot}/\bar{C}_{tot,\infty} = 0.5$ and see an intersection with the infinite bath timecourse at $D^*t/R^2 = 0.03$. At this juncture we need to specify some of the properties of the chemicals and sediments. Suppose we have a particular PCB congener with $\log K_{ow} = 7$ and $D_w = 7 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, as well as a particular silty sediment of 100- μm diameter and organic carbon content of 4%. Assuming these dredged sediments also exhibit $\phi \cdot f \approx 0.02$ (as reported by Wu and Gschwend, 1986 for a few samples), we now calculate the time to 50% release of the PCB of interest:

$$t_{50\%} \approx 0.03 R^2 / D^* \quad (11-166)$$

$$\approx \frac{(0.03)(R^2)(\rho_s(1-\phi) \cdot f_{oc} \cdot K_{oc} + \phi)}{\phi f \cdot D_w} \quad (11-167)$$

$$\approx \frac{(0.03)(50 \cdot 10^{-6} \text{ m}^2)(2 \times 10^3 \text{ kg/m}^3 \cdot 0.04 \cdot 3.1 K_{ow}^{0.72} \times 10^{-3} \text{ m}^3/\text{kg})}{(0.02 \cdot 7 \cdot 10^{-10} \text{ m}^2/\text{s})}$$

$$\approx 1.5 \cdot 10^5 \cdot \text{s}^{-1} \text{ or about 2 days}$$

where we assume a bulk density ($= \rho_s(1-\phi)$) of $2 \text{ g} \cdot \text{cm}^{-3}$. Note that $[\rho_s(1-\phi)K_d]$ is much greater than any reasonable value of ϕ , so the porosity in the numerator can be neglected in our calculations. Since the time of release appears similar to that time expected for such spilled dredge particles to fall back to the bottom, one should expect a substantial release of even hydrophobic PCB congeners, but not equilibration.

Other Issues of Sorption Kinetics

The situation in which mass transfer into and out of aggregates limits the rate of sorptive exchange may be common, but this conceptualization will not cover every case where mass transfers are controlling. As alluded to earlier, sometimes the slowest process controlling sorption of organic molecules of interest to us involves their movements through pores of similar size to themselves (e.g., Wood et al., 1990; Ball and Roberts, 1991). If this is the case, we must reduce D in mass balance equations like Eq. 11-153 even further using a constrictivity factor (Satterfield et al., 1973). It is also possible that diffusion in small continuous pores occurs, not only in the water filling the pores, but also on the walls themselves (i.e., surface diffusion). Release of organic contaminants from these positions within the solids may require months to years (Coates and Elzerman, 1986; Steinberg et al., 1987; Pavlostathis and Jaglal, 1991).

Another possibility is that molecular diffusion into macromolecular organic matter may be the slowest step in the overall process in some cases (Brusseau et al., 1991; Brusseau and Rao, 1991). Due to the relatively "viscous" nature of such organic matter, the diffusion coefficients of organic sorbates moving in this polymeric matter may be significantly lower than comparable free-solution values. If the diffusion pathlengths are long enough, transfer of hydrophobic compounds into all parts of the humus of soils and similar media on other particles may control the overall sorptive exchange rate.

Until now, we have considered only linear partitioning of sorbates at each microscopic position within an aggregate. Obviously, some sorption mechanisms require us to examine cases of nonlinear surface-solution exchange. Such a case was considered in the uptake of alkyl benzene sulfonates by porous granular carbon particles (Weber and Rumer, 1965). In this situation $C'_s(r)$ was related to $C'_w(r)$ using a Langmuir isotherm to yield a result comparable to what we reached with Eq. 11-147.

We conclude this discussion of sorption kinetics by noting that the concepts of mass transfer limitation we have discussed are general. Their application to many situations, with appropriate modifications, will undoubtedly prove effective. A recent example of this is provided by Rounds and Pankow (1990), who successfully characterized organic vapor molecule-atmospheric particle exchange kinetics with a radial diffusion model.